A THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

THE THERMAL DECOMPOSITION OF SOME SILPHENYLENE-SILOXANE POLYMERS

BY

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Sheila R. Beattie

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ABBREVIATIONS

USED THROUGHOUT THE THESIS

DMS	poly(dimethylsiloxane)
MPPS	poly(methylphenyl-p-silphenylene-siloxane)
THF	tetrahydrofuran
TMAH	tetramethylammonium hydroxide
TMG	tetramethylguanidine di-2-ethylhexoate
TMPS	poly(tetramethyl-p-silphenylene-siloxane)
TMPS/DMS	poly(tetramethyl-p-silphenylene-siloxane/ dimethylsiloxane)
TPPS	poly(tetraphenyl-p-silphenylene-siloxane)

SUMMARY

Polymers composed of alternating p-silphenylene and siloxane units with either dimethyl or methylphenyl substituted silicon atoms have been prepared in a dilute solution condensation of the appropriately substituted phenylenedisilanol, catalysed by tetramethylguanidine di-2-ethylhexoate, TMG. A range of copolymers has been synthesised with extended siloxane segments where the substituents on the silicon atoms are both methyl groups. Two methods of polymerization have been employed with comparable success. These are the condensation between p-phenylenebis(dimethylsilanol) and tetramethyldisiloxanediol catalysed by TMG and the KOH catalysed polymerization of p-phenylenebis(dimethylsilanol) and octamethylcyclotetrasiloxane. Characterisation of the polymers employed the techniques of infrared and n.m.r. spectroscopy and membrane osmometry. Attempts to prepare poly(tetraphenyl-p-silphenylene-siloxane), TPPS, with a high molecular weight have met with little success, only low molecular weight polymer being obtained.

The first feature observed in the thermal degradation of poly(tetramethyl-p-silphenylene-siloxane), TMPS, is the development of insolubility in the residue when the polymer is heated isothermally at 350-400°. Weight loss is slight at this stage and is due to the formation of the cyclic dimethylsiloxane trimer and tetramer and a small quantity of "cold ring" fraction. It is suggested that the mechanism at this stage involves structural rearrangements leading either to chain

branching or some production of volatile material.

Prolonged heating of TMPS at 450-500° results in up to 80% weight loss, most of which is collected as "cold ring" fraction. Subsequent separation and analysis using GC, GCMS and infrared spectroscopy identified a series of short chain oligomers terminated by either the Si-H or the Si-Ph group. A mechanism involving direct scission of the silphenylene bond has been proposed to account for their formation.

The products of degradation of the silphenylene-siloxane polymers with extended siloxane segments are dependent on the copolymer composition. A complex mixture of cyclic oligomers has been separated and identified from the"cold ring" fraction of those polymers with low silphenylene content. The presence of these compounds at the lower temperatures of degradation has led to the assumption that their formation involves a structural rearrangement not unlike that involved in the degradation of poly(dimethylsiloxane), DMS. Results from infrared analysis demonstrates that Si-H groups are formed at higher temperatures, indicating the occurrence of silphenylene bond scission. As the silphenylene content increases, the characteristics of degradation become increasingly more like those observed for TMPS. Thus both the range and the amount of cyclic oligomers, formed in structural rearrangements, decreases in favour of the formation of linear oligomers via rupture of the silphenylene bond.

One feature common throughout the copolymer series is the chain branching reaction occurring between 350 and 400°. A comparison of the rates of branching, calculated from sol-gel analysis, has shown that the rate is directly proportional to the

silphenylene content.

Thermal analysis demonstrates that poly(methylphenyl-p-silphenylene-siloxane), MPPS, is thermally more stable to weight loss than TMPS. Benzene and a mixture of linear oligomers, similar in structure to the original polymer but with Si-H and Si-Ph end-groups, have been analysed and identified as the volatile products of degradation with the aid of GC, GCMS and infrared spectroscopy. No evidence of cyclic compounds has been detected. A comparison of results calculated from sol-gel analysis reveals that chain branching occurs more rapidly in MPPS than TMPS.

Two distinct stages again appear to be present in the degradation of MPPS. At the lower temperatures of degradation structural rearrangements are responsible for chain branching and the initial production of benzene. Increasing the temperature causes the mechanism to undergo a change to one involving scission of either the silphenylene or Si-Ph bond as the first stage. Further production of benzene and the formation of the short chain oligomers occur in the higher temperature range.

Results from TG demonstrate that the low molecular weight TPPS is thermally less stable to weight loss than DMS. Apart from benzene all the products of degradation are contained in the "cold ring" fraction. Infrared analysis demonstrates that these products are similar in structure to the original polymer. However in view of the inability to obtain high molecular weight polymer, further investigations of the thermal degradation properties of TPPS have not been pursued.

To conclude this work two dimethyl substituted aryloxysilane polymers have been synthesised in a melt polymerization of

dimethyldianilinosilane with either hydroquinone or bisphenol A. The thermal stabilities of these polymers have been investigated briefly to gain some indication of the potential value of a more detailed study in this field. Although their thermal stability to weight loss is less than the silphenylene-siloxane polymers, it is comparable with that of DMS. Thus a more thorough investigation of the thermal degradation behaviour of the aryloxysilane polymers has been recommended.

CHAPTER 1

INTRODUCTION

1.1. General Introduction

Although interest in silicon chemistry began in the 1820's when Berzelius, the Swedish chemist studied the structure of silica, it was not until 1872 that Ladenburg in Germany was the first to observe the formation of a polysiloxane oil obtained in the hydrolysis of diethyldiethoxysilane. Early in the 20th century Kipping set out to show how the chemistry of silicon resembled that of carbon. He prepared a wide range of derivatives but neglected the heavy, viscous by-product, in which the Si-O-Si linkage was observed, as he could foresee no future for this compound.

Commercial interest began in the 1930's when Hyde of the Corning Glass Works perfected the technique of processing silica to polysiloxanes. Corning, recognising the potential of these polymers, amalgamated with the Dow Chemical Company to manufacture the first commercial siloxanes in 1942. Dow Corning's first product was a water repellent, used in the insulation of ignition and electrical systems in internal combustion engines. This grease-like compound protected aero engines against failure due to water thus saving untold numbers of aircrew lives and indicating the potential value of siloxane polymers in the future.

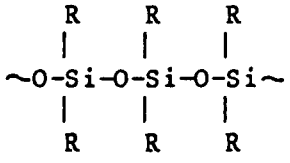
Meanwhile in the USSR, Andrianov's interest in Kipping's work had been aroused. He was able to associate Kipping's viscous by-product with the Si-O-Si linkage in silicates. In 1937 he demonstrated that polymers with alternating silicon and oxygen atoms in the backbone could be prepared (Ref 1). This marked the beginning of an extensive research programme on siloxane related polymers at the Soviet School of Chemists under his supervision. However, it was not until 1947 that the fist commercial polysiloxane was prepared in the USSR.

Since their commercial birth in 1942, the polysiloxanes have found increasingly more widespread use. Table 1.1 lists a few of these. Their diversity of application may be attributed to two main factors. Not only do they possess a combination of properties which is almost unique but also the number of possible structural modifications is almost unlimited.

Field of Use	Main Application
Car Industry	Hydrolic or damping fluids Polishes
Surgery	Prosthetic parts Lubrication of instruments
Chemical Industry	Antifoaming Sealing
Space Exploration	Heat shields protecting the Gemini capsules
Building Industry	Water repellent treatments
Pharmaceuticals	Creams, ointments Adhesive tapes
Rubber Industry	Cable making Manufacture of synthetic rubber
Cosmetics	Toothpaste Powders Shampoos
Ship Building	Metal protection
Household	Non-stick treatment of pans Polishes and cleaners

TABLE 1.1

Linear polysiloxanes may be represented by the general formula,



where R may be almost any organic radical but is in practice usually the phenyl or methyl group. Replacing methyl by phenyl groups results in increased resistance to temperature variation and improved compatability with organic compounds but the fluidity decreases. By varying the degree of crosslinking a wide range of materials becomes available from the non-crosslinked fluids to the partially crosslinked gels and rubbers and the highly crosslinked solid resins. Other interesting variations involve the replacement of varying amounts of either the silicon or oxygen atoms or groups such as Al, Tl, Sn or N atoms or methylene or ethylene groups.

Polysiloxanes may be regarded as intermediate between organic polymers and inorganic silicates. They comprise an inorganic backbone of alternating silicon and oxyen atoms with organic radicals attached to each silicon atom. The Si-O bond, to which there is no analogue in nature, retains some of the thermal stability and chemical inertness of the silicon-oxygen skeleton found in quartz and silica.
The partial oxidation of silicon in the siloxane unit to SiO_2 leads to the high resistance of this link to oxidation and to the non-flammability of the siloxane polymers. The presence

of organic radicals is responsible for their outstanding water repellency. Other properties worth noting are low dependency of physical properties on temperature, high electrical resistance, ability to defoam, non-toxicity and good resistance to radiation.

1.2. Polymer Degradation (General)

Thermal degradation studies are an essential part of assessing the potential value of new polymers. In general polymers are organic compounds which, due to their high molecular weight, possess the necessary properties for use as fibres, plastics and rubbers. An apparently attractive polymer may undergo changes in molcular weight when exposed to say heat or light, with a resultant change in the physical form which would render it unsuitable for its intended application.

In a chain scission reaction one break per chain would effectively half the average molecular weight of the polymer. Similarly the formation of one crosslink would double the molecular weight. Since each polymer molecule may contain many hundreds of monomer units, it appears that a very small extent of reaction may have a large effect on the molecular weight and consequently on the physical properties.

The nature of the products formed in the degradation reaction must also be determined. The release of toxic compounds where the intended application is in the food industry requires no further elaboration.

The term "polymer degradation" refers in this context to any chemical change undergone by the polymer irrespective

of the effect on the physical properties. In processing a raw polymer, techniques such as moulding or extrusion may be necessary to form a useful material. To do this, the polymer is exposed to the degradation agencies of heat, oxygen and mechanical stress. Throughout its useful life many other external forces act on the polymer. These include light, high energy radiation, ozone, atmospheric pollutants (especially SO_2 and NO_2) and other chemical compounds. Depending on the application, a material is frequently subjected to more than one of these forces simultaneously. It is, however, convenient to study the effects of each in isolation.

Polymer degradation reactions may involve either the backbone or the substituent atoms or groups. A chain scission or depolymerization reaction causes a decrease in molecular weight and/or formation of volatile products. These volatile materials are typically chain fragments in which monomer units are recognisable. An increase in molecular weight or formation of insoluble material suggests crosslinking. Volatile compounds formed in a substituent reaction not involving the backbone are quite different from the monomer unit. When the loss of a substituent group involves radical formation it is not uncommon for chain scission or crosslinking to be induced. Side groups reacting together without formation of volatiles may

also alter the physical properties.

Degradation studies are of considerable academic interest, being a useful tool in the study of the chemistry of new polymers. From such studies the products of degradation may be identified and the kinetic and thermodynamic parameters of the reaction derived. A knowledge of the mechanism may provide the information necessary to indicate how an existing polymer may be modified or a new polymer synthesised to meet the required stability. It is always hoped that from these studies a polymer of potential commercial development will emerge.

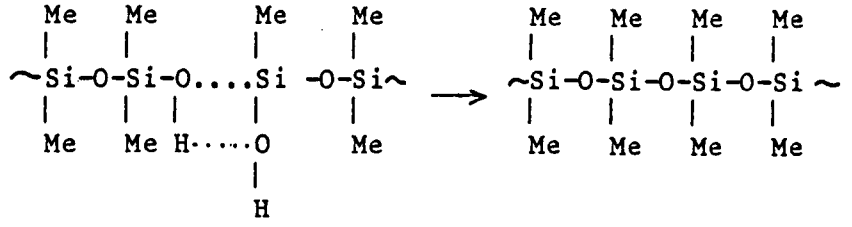
1.3. Thermal Degradation of Siloxane Polymers

In common with most inorganic polymers, the thermal stability of the siloxane polymers is lower than predicted from bond dissociation energies alone. This is due to less energetic mechanisms such as structural reorganisations being available to this class of polymers. An understanding of the mechanism of these low energy pathways is essential if it is wished to prepare a polymer of improved stability.

1. Poly(dimethylsiloxane) (DMS)

The first change observed on degrading a sample of hydroxyl terminated DMS is an increase in the intrinsic viscosity (Ref 2). This occurs before the onset of evolution of volatile products and was explained by an increase in molecular weight.

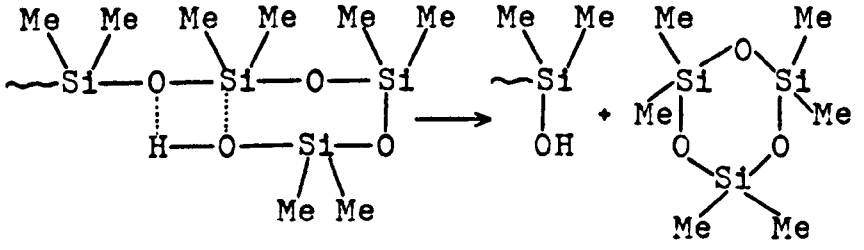
Measurements of the molecular weight made by Grassie and Macfarlane (Ref 3) confirmed this explanation. It was proposed that it could be accounted for by an intermolecular condensation of hydroxyl groups.



$+ H_2O$

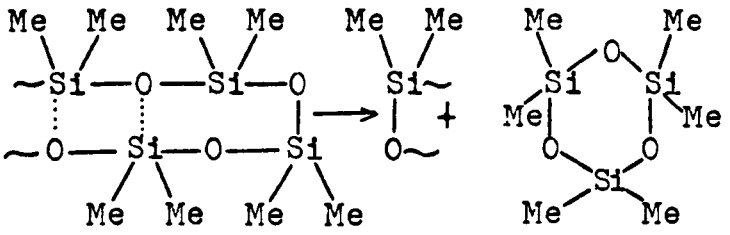
When DMS is heated under vacuum, evolution of volatile material commences at 343° (Ref 2). Patnode and Wilcock (Ref 4) in 1946, were first to identify these products as a continuous series of cyclic oligomers from trimer upwards, trimer being the most abundant product. No other products were observed.

After discovering that the rate of depolymerization depends on the nature of the end groups, Aleksandrova et al (Ref 5) proposed the following mechanism:



Examination of the thermal degradation of DMS containing various end-groups showed that the rate of depolymerization is decreased when the terminal hydroxyls are replaced by methyl groups (Ref 2).

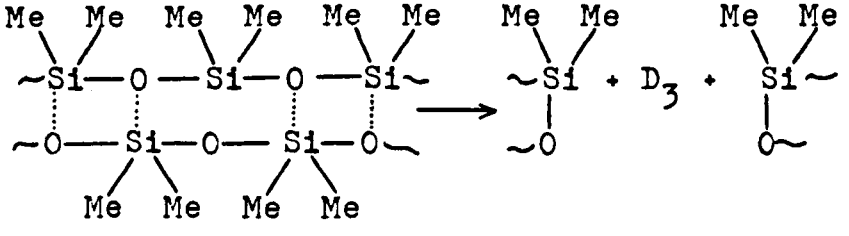
End blocking does not however affect the nature of the products (Ref 3). To account for this Thomas and Kendrick (Ref 6) put forward a mechanism not unlike that proposed by Aleksandrova.



Therefore the formation of the cyclic transition state is facilitated by the presence of the hydroxyl end groups.

Molecular weight measurements of the hydroxyl terminated polymers show an initial increase followed by a decrease which is linear with the extent of weight loss (Ref 3). This is not unexpected if production of volatiles occurs in the stepwise manner suggested by the above mechanisms. A decrease in molecular weight more rapid than the linear relation with volatile formation would have indicated a chain scission reaction (Ref 7).

The possibility of DMS undergoing an intermolecular rearrangement was suggested by Neilson (Ref 8):



As previously observed in the intramolecular rearrangements, this mechanism involves nucleophilic attack at silicon by oxygen to form a cyclic transition state. In an attempt to obtain some evidence for this theory Grassie and Francey (Ref 9) degraded a blend of DMS and poly(methylphenylsiloxane). The formation of large yields of cyclic products containing both dimethyl and methylphenyl substituted silicon could only be explained by an intermolecular process of this type.

2. Polysiloxanes with phenyl substituents.

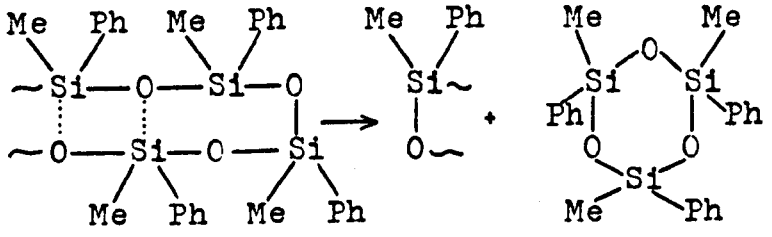
Comparison of the thermal degradative behaviours of poly(dimethylsiloxane) (Ref 3) and poly(methylphenylsiloxane) (Ref 10) has demonstrated that the replacement of methyl by phenyl groups in siloxane polymers results in an increase in stability. Some workers have accounted for this on the basis of steric considerations while others maintain that the electronic effect of the phenyl group is the critical factor.

Andrianov has suggested that the spiral structure of DMS favours the formation of the cyclic transition state (Ref 2). The presence of the bulky phenyl group inhibits the tendency for the polymer molecules to form a spiral structure thus hindering the depolymerization reaction. When Kovalenko et al

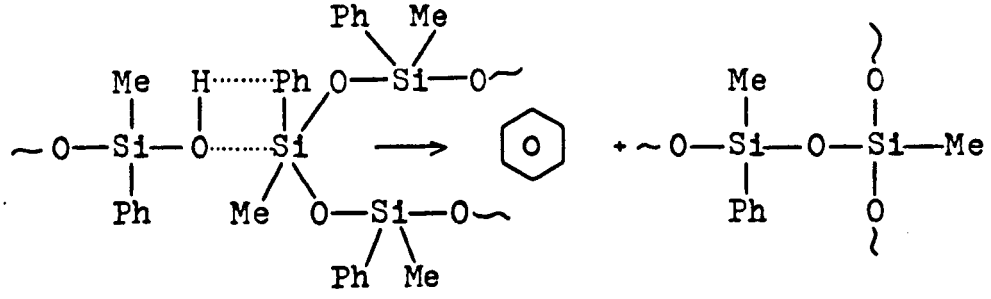
(Ref 11) studied the thermal stability of branched DMS it was found that an increase in the number of branches resulted in an increase in the stability of the polymer. This again suggests that the ability of the siloxane molecule to form a spiral structure is critical.

An alternative approach is to consider the electronic effect of the phenyl group attached to silicon atoms. Noll (Ref 12) attributes the increased stability to the electron withdrawing effect of the phenyl group strengthening the Si-O bond. However, results from other sources (Ref 13,14) state that when attached to silicon the phenyl group is electron donating due to interaction between the empty d orbitals on silicon and the $p\pi$ delocalised electron system of the phenyl group.

Thomas and Kendrick (Ref 13) degraded samples of trimethylsilyl terminated poly(methylphenylsiloxane) isothermally at 400° under vacuum. The various isomers of the cyclic trimer and tetramer were identified as the sole products. A transition state mechanism analogous to that in the DMS degradation was invoked:

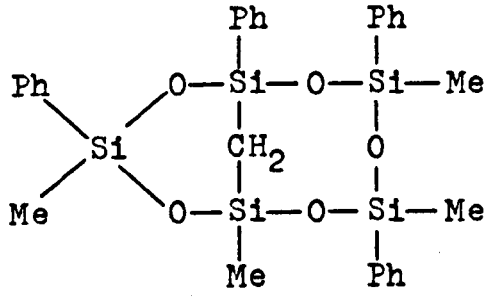


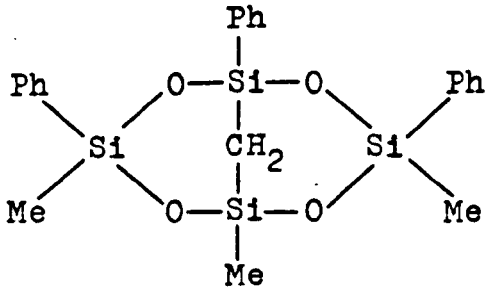
End-blocking or increasing the molecular weight of hydroxyl ended poly(methylphenylsiloxane) reduces the thermal stability (Ref 10). Chubarov (Ref 15) suggested the following mechanism in which the hydroxyl end groups participate in a chain branching reaction which will in turn inhibit formation of cyclics.



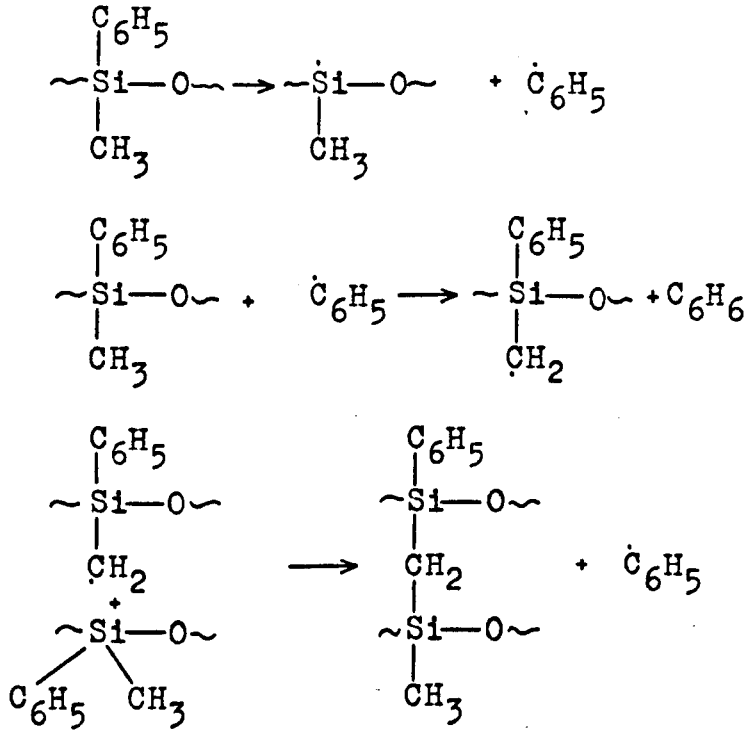
The appearance of small quantities of benzene at 300° supports this mechanism (Ref 10).

Increased benzene production and the appearance of two bicyclic oligomers (Ref 10):





at 500° suggested that the mechanism changes from one of rearrangement to a radical scission process. Sobolevskii (Ref 16) proposed a free radical sequence which explains both the formation of the methylene bridges and the production of benzene:



Further degradation leads to the formation of bicyclic compounds.

Poly(dimethyl/methylphenylsiloxane) copolymers yield benzene and siloxane ring compounds on thermal degradation (Ref 9). As in poly(methylphenylsiloxane) benzene is produced at 300° in a rearrangement reaction involving hydroxyl groups and at 500° in the random scission of the Si-Ph bond. Bicyclic compounds also appear at 500°. When the methylphenylsiloxane content is low the degradation behaviour resembles that of

DMS in so far as end-blocking enhances the stability. Increasing the methylphenyl content results in a decrease in the stability of the trimethylsilyl end-grouped polymers relative to those with hydroxyl terminals. No new mechanisms were considered to account for the degradation of these poly(dimethyl/methylphenylsiloxane) copolymers.

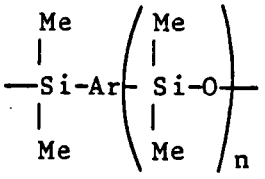
The products from the thermal degradation of poly(dimethyl/diphenylsiloxane) consist of benzene and a complex mixture of cyclic oligomers (Ref 17). Since the mechanisms discussed in the degradation of DMS, poly(methylphenylsiloxane) and poly(dimethyl/methylphenylsiloxane) are valid, they require no further mention here.

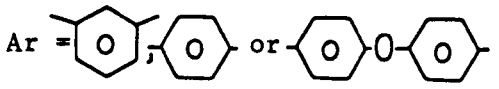
3. Silarylene-siloxane polymers

The effect of replacing varying amounts of oxygen atoms with arylene groups in the linear polysiloxane is also of interest. Several advantages result from the inclusion of silarylene units in the polymer backbone, including an increase in the crystallinity, viscosity, viscosity-temperature coefficient and thermal stability (Ref 18). The enhancement of the thermal stability has been attributed to the arylene group lowering the chain flexibility which in turn curtails formation of cyclics (Ref 19). Attempts made by Merker and Scott (Ref 20) to prepare the cyclic tetramethyl-p-silphenylene-siloxane dimer and trimer

have demonstrated this reluctance to form cyclic structures.

Thermogravimetry of silarylene-siloxane polymers with the general structure

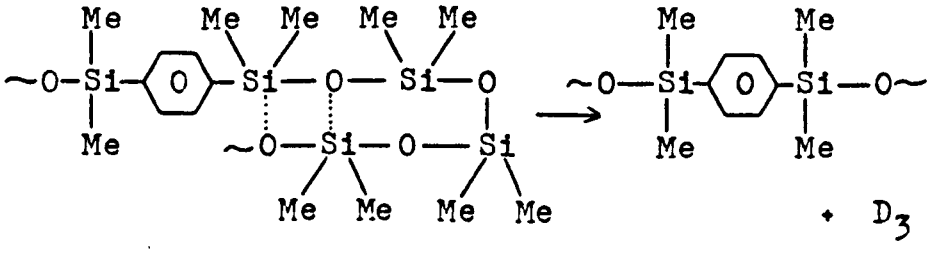




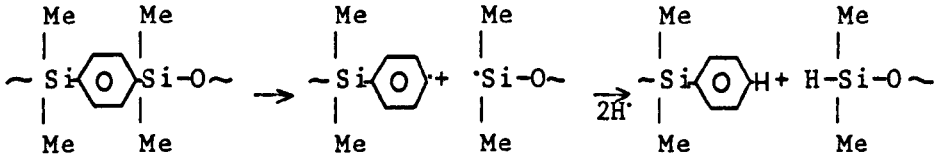
n = 1-4

illustrates that the heat stability depends on both the identity of the arylene group and the length of the dimethylsiloxane chain segments (Ref 21,22,23). The polymer containing the p,p'-phenyleneoxyphenylene units had the greatest thermal stability while that with the m-phenylene was least. As the length of the siloxane chain segment increases the thermal stability falls. However, large values of n may be accommodated before the decomposition mechanism effective in DMS limits the stability of the polymer (Ref 23).

Korshak and Vinogradova (Ref 19) suggest that in the thermal degradation of silarylene-siloxane polymers formation of cyclics proceeds along the siloxane chain segment but is terminated upon reaching a silphenylene unit.

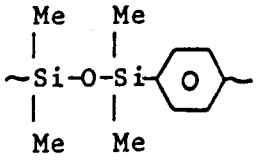


At temperatures above 450°, scission of the silphenylene bond was assumed to become the predominant mechanism (Ref 21) instead of the rearrangement as in DMS.



Although no evidence was given to support this mechanism it is not unlike that proposed by Sobolevskii to account for the thermally induced changes in oligomethylphenylsiloxanes (Ref 16).

Vada and his co-workers (Ref 21) degraded poly(tetramethyl-p-silphenylene-siloxane),



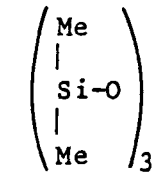
at 500° for 3 h and collected the pyrolysis products. These were identified as hydrogen, methane, ethane, ethylene, dimethylsilane, tetramethyldisiloxane and compounds containing Si-H and Si-C_6H_5 groups. It was claimed that degradation via silphenylene bond scission was the only process involved.

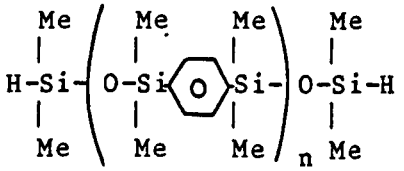
Funt et al (Ref 24) compared the thermal stabilities under nitrogen of some poly(tetramethyl-p-silphenylene-siloxane/dimethylsiloxane), TMPS/DMS, copolymers with those of the two homopolymers poly(tetramethyl-p-silphenylene-siloxane), TMPS, and

DMS. Thermogravimetry up to 800° illustrated that two distinct reactions occur in the decomposition. This was contrary to the results of Andrianov (Ref 25) and Breed et al (Ref 23) who observed only one component in the TG curves. The activation energies of the two phases in the TG traces were calculated to be 44 and 13 kcal mol^{-1} respectively and were noted to be independent of both molecular weight and p-silphenylene content. DMS itself decomposes on heating with an activation energy of 44 $\pm$ 3 kcal mol^{-1} with a second reaction occurring in the presence of residual catalyst at 15 $\pm$ 1 kcal mol^{-1} (Ref 6). The close agreement of the activation energies for TMPS, DMS and the copolymers led to the proposal that similar mechanisms featured in each case, that is scission of the siloxane bond. The volatile products consisted mainly of the cyclic dimethylsiloxane trimer and the monomer and dimer of tetramethyl-p-silphenylene-siloxane as predicted from the mechanism suggested.

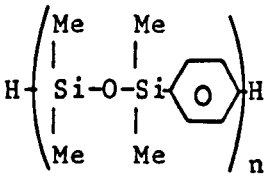
In a more recent publication, Zelei et al (Ref 26) listed the following products from pyrolysis gas chromatography of TMPS carried out at 500° under argon:

CH_4 , C_6H_6

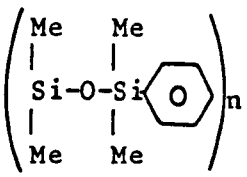




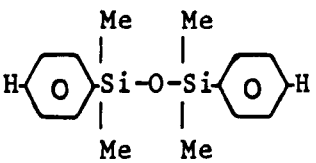
n = 0,1,2



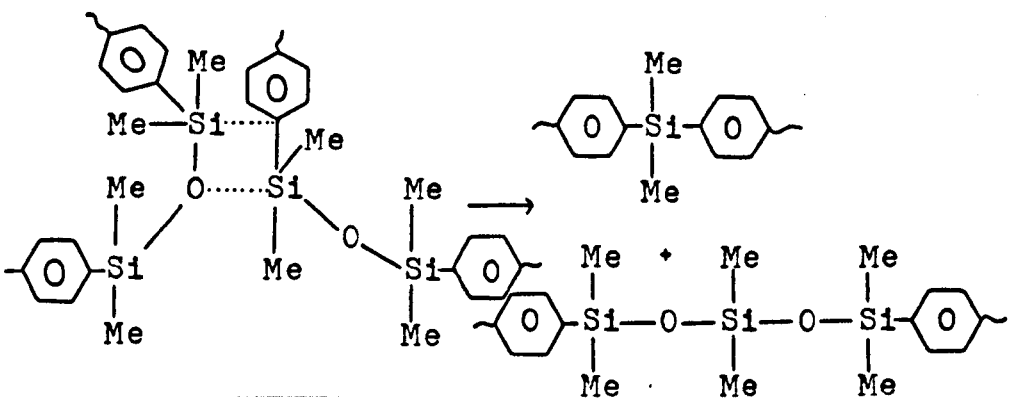
n = 1,2



n = 2,3



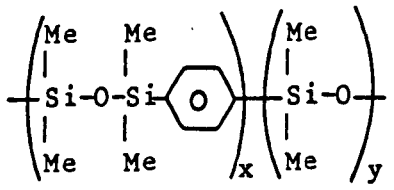
It was claimed that the presence of cyclic oligomers typified a siloxane type of rearrangement. However the low yields of these cyclics reflected the reduced chain flexibility relative to DMS. An intermolecular rearrangement mechanism involving more than one stage was invoked to form the hexamethylcyclotrisiloxane.



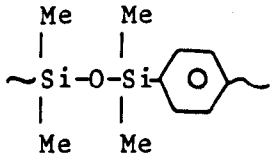
The main degradation involved scission of the polymer backbone at the Si-C bonds. The radicals formed are terminated by hydrogen possibly abstracted from the methyl groups. The close resemblence of the infrared spectrum of the insoluble residue to that of poly(phenyl-silsesquioxane) suggested that the siloxane chains were crosslinked by oxygen atoms or p-phenylene groups. No explanation was given for the fate of the methylene radicals or the formation of methane.

1.4 Aim of this Work

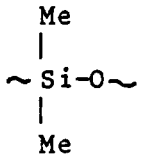
This project is concerned with the synthesis and subsequent study of the thermal degradation of specific polysiloxanes where the oxygen atoms have been replaced in varying degree by p-phenylene units, the organic substituents on silicon being either the phenyl or methyl group. The effect of the p-phenylene unit will be investigated in a comparative study of the thermal decomposition of a series of random poly(tetramethyl-p-silphenylene-siloxane/dimethylsiloxane), TMPS/DMS, copolymers of the general structure,



with those of poly(tetramethyl-p-silphenylene-siloxane), TMPS,



and poly(dimethylsiloxane), DMS,



The dependence of the thermal stability on the nature of the organic substituent will be considered in the decomposition of poly(methylphenyl-p-silphenylene-siloxane). The ultimate aim is to gain an insight into the degradation reaction mechanisms.

CHAPTER 2

EXPERIMENTAL TECHNIQUES

2.1. Synthesis and Characterisation

Monomer and polymer preparations are given in detail in Chapter 3 together with results, such as infrared and n.m.r. spectra, which are necessary for polymer characterisation.

2.2. Thermal Analysis

(1) Thermogravimetry (TG)

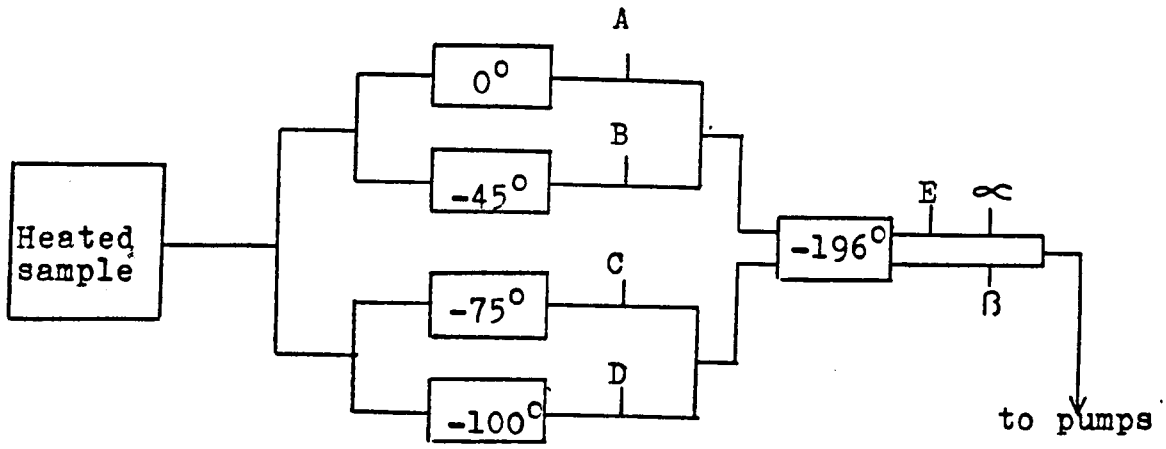
A Du Pont 951 instrument was used for the thermogravimetric measurements. A change in the mass of a sample is measured as a function of a programmed rise in temperature. In all cases a 10 mg sample was heated at a rate of 10°min^{-1} in a constant velocity nitrogen stream (60 ml min^{-1}).

(2) Differential Scanning Calorimetry (DSC)

DSC was carried out using a Du Pont 910 differential scanning calorimeter. Samples (5 mg) were heated in an aluminium DSC pan at 10° min^{-1} in a dynamic atmosphere of oxygen free nitrogen from ambient temperatures. A similar empty aluminium pan was used as a reference.

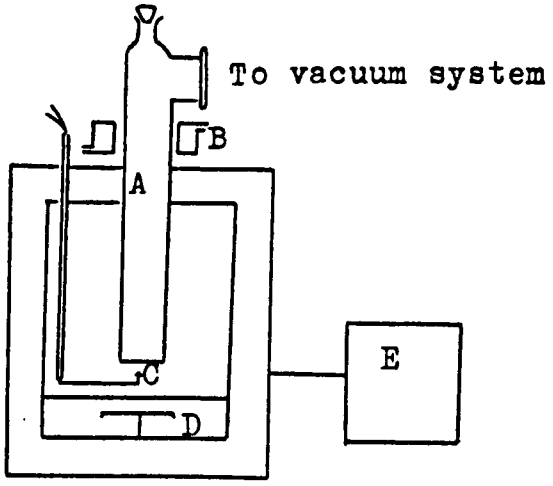
(3) Thermal Volatolisation Analysis (TVA)

Differential condensation thermal volatolisation analysis, as developed by McNeill (Ref. 27), is a powerful tool in the study of polymer degradation. By measuring the pressure of volatile materials produced during the degradation process, information on the reaction rate may be obtained. A schematic diagram of the general experimental layout used in this study is given in Figure 2.1.



∝, β are sample collection points.
A-E are Pirani gauge heads. A-D are equidistant to oven and -196° trap.

Fig. 2.1a) TVA apparatus



A Pyrex glass degradation tube.
B 'Cooling jacket'.
C Chromel-alumel thermocouple.
D Oven fan.
E Temperature programmer.

Fig. 2.1b) TVA heating assembly.

A polymer sample is placed on the base of a degradation tube and heated using a Perkin-Elmer F11 oven, equipped with a linear temperature programmer, from ambient to 500° at a rate of $10°min^{-1}$. The top of the tube and the greased flange joint are maintained at ambient temperatures by means of a cold water jacket or "cold ring". A chromel-alumel thermocouple, fixed near the base of the tube monitors the oven temperature. The vacuum line is pumped continuously throughout the experiment.

As the sample is heated, volatile degradation products are released and pumped via four geometrically equivalent routes towards a common back-up trap at -196°. Only those products which are sufficiently volatile to pass through a given trap will effect a response on the corresponding Pirani gauge head. Outputs from the respective Pirani heads are transmitted via a multihead switch unit to a 12 channel recorder, where they are recorded simultaneously with the oven temperature. Since one or more of the products may condense on reaching a given trap, these outputs are frequently non-coincident.

The products may be analysed conveniently in three fractions:

(a) the involatile residue which remains in the degradation tube,

(b) products volatile at degradation temperatures but involatile at ambient temperatures ("cold ring" fraction), which collect on the cold upper part of the degradation tube,

(c) products volatile at ambient temperatures but

involatile at the cold trap temperatures (condensables), and which are recorded by the Pirani gauges in the TVA experiment.

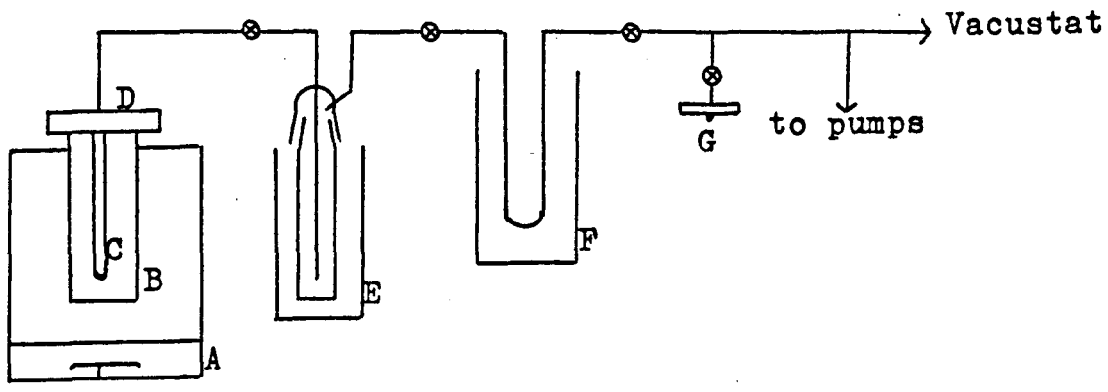
The "condensables" may be collected for further analysis by subsequent distillation into a suitable collecting vessel such as an ir gas cell. Rinsing the degradation tube with a suitable solvent allows the "cold ring" fraction to be removed. Techniques such as GC, GCMS and infrared spectroscopy were used to characterise this fraction. Infrared spectra of the involatile residue were recorded using the KBr disc technique.

(4) Vacuum Line Degradation System

Figure 2.2. illustrates the experimental apparatus used to study the behaviour of the polymers when they are heated isothermally in a continuously pumped high vacuum system.

A weighed sample contained in a small glass vessel was placed at the bottom of the degradation tube. The tube was evacuated to 10^{-6} torr and heated by a Perkin-Elmer F11 oven to the required temperature for a set period of time. The oven temperature was measured with a chromel-alumel thermocouple.

The degradation products were divided into fractions for analysis according to their volatility. The fraction which condensed only at -196° was distilled subsequently into a gas cell and the infrared or ultraviolet spectra recorded. Compounds involatile at ambient temperatures or at -70°C were collected by rinsing the cold finger or initial trap with a suitable solvent such as diethyl ether, toluene or carbon tetrachloride. GC, GCMS and infrared spectrometry proved to be the most valuable tools for



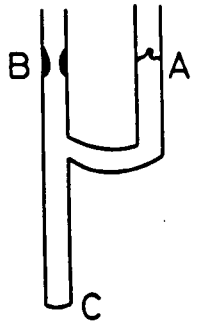
A PE F11 oven.
B Degradation tube.
C Cold finger.
D Water cooled jacket.
E -70° trap.
F -196° trap.
G Gas cell.

Fig. 2.2 Vacuum line degradation system.

their identification.

The polymer residue was examined in several ways. Infrared spectra were recorded either on thin films cast on sodioum chloride salt plates or using the KBr disc technique. Molecular weights were measured of residues from degradation at lower temperatures. Increasing the temperature of degradation rendered the residue insoluble. Sol-gel analysis was carried out and the results were analysed using the Charlesby-Pinner equation (Ref.28).

(5) Closed System Degradation



In the apparatus shown, the sample was introduced into C via constriction B, before sealing at B under high vacuum. This enables degradation of the polymer without loss of any non-condensable gases. These may be released through the break seal at A and collected for analysis.

2.3. Analytical Techniques

(1) Infrared Spectroscopy

Infrared absorption spectra were obtained using either a Perkin-Elmer 257 grating infrared spectrophotometer or a Pye Unicam SP3-100 instrument.

Polymer samples were prepared as thin films on sodium chloride discs. The films were cast from diethyl ether solution.

The polymer residue and those products found on the cold

finger after degradation were examined either as a thin film cast from diethyl ether solution or in a KBr disc.

The volatile products were collected in a gas cell 95 mm long with sodium chloride windows. This could be placed directly in the path of one of the infrared beams and the spectrum recorded.

(2) Nuclear Magnetic Resonance Spectroscopy

Proton magnetic resonance spectrometry provides a useful tool in the identification and structural analysis of organosilicon compounds. Structural analysis of siloxane related compounds is aided by the fact that the Si-Me resonance is generally a sharp singlet so that non-equivalences are more easily detected. The chemical shift of the Si-Me group when it is situated between two oxygen atoms is sufficiently different from that between an oxygen and a p-phenylene group for both resonances to be resolved. This is illustrated in Figure 2.3 and the protons responsible for each signal are listed in Table 2.1.

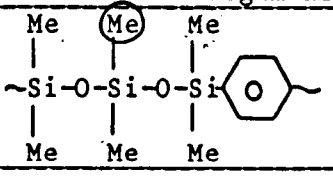
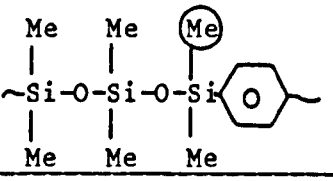
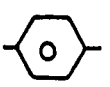
τ Value ppm	Signal	Assignment
9.77	Singlet	
9.49	Singlet	
2.34	Singlet	

TABLE 2.1

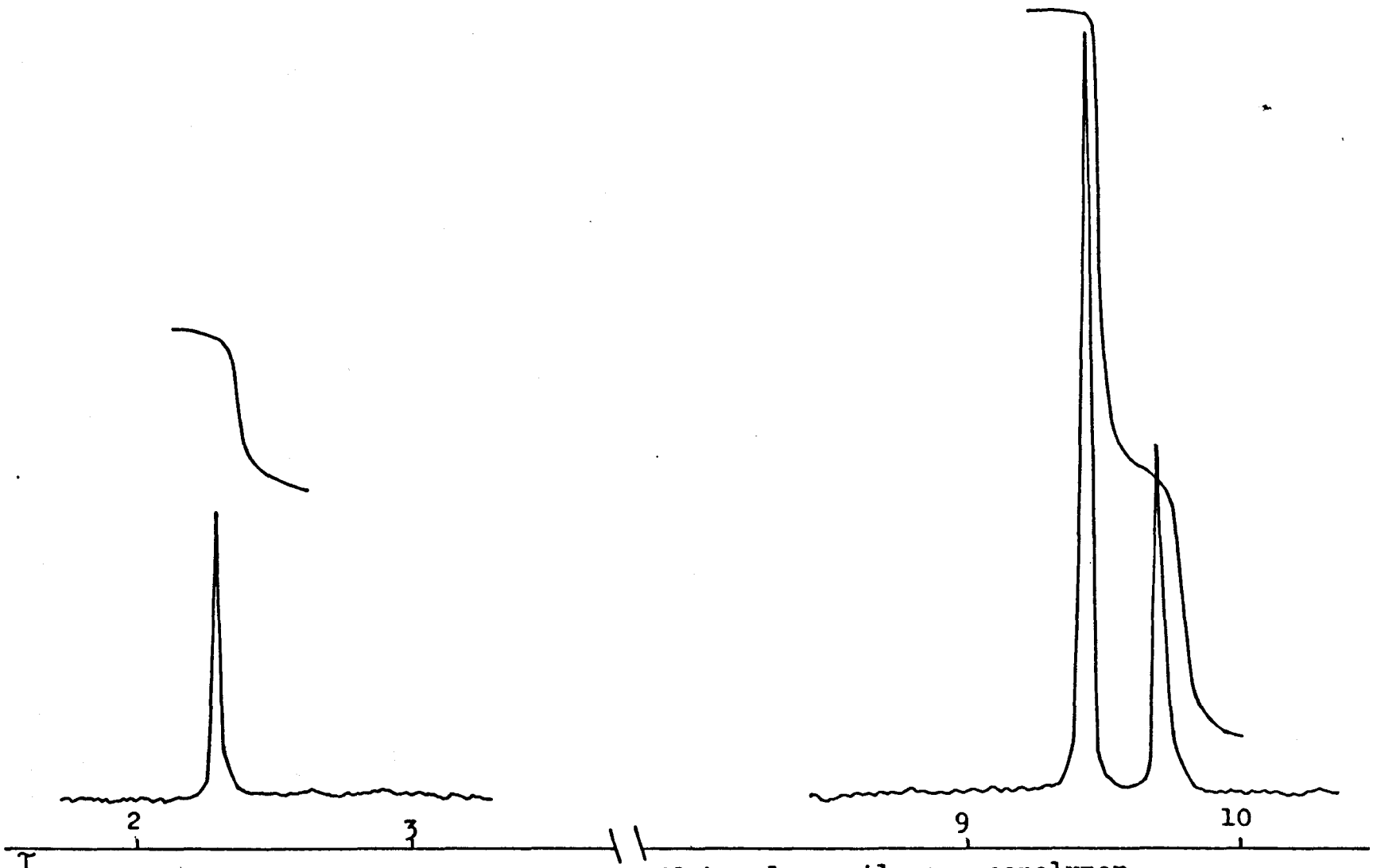
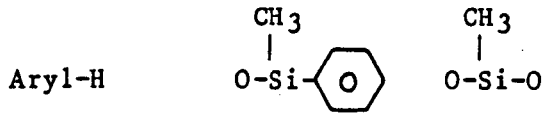
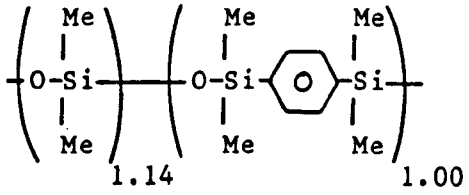


Fig. 2.3 Typical n.m.r. spectrum of a silphenylene-siloxane copolymer.

Integration allows measurement of the molar ratios of the respective Si-Me groups and hence the bulk composition of the different copolymers may be determined. Thus for the example given in Figure 2.3., the relative intensities of the signals are:-



The bulk composition of this copolymer would be given by the structure



Spectra were recorded on either a Perkin-Elmer 32 (90MHz) or a Varian T60 (60MHz) spectrometer. The samples were dissolved in carbon tetrachloride or deuterated acetone. No internal reference was used.

(3) Ultraviolet Spectroscopy

A Unicam SP800 spectrophotometer was used to record ultraviolet spectra. In the present work the use of ultraviolet spectroscopy was limited to the search for benzene as a possible product of degradation. Samples were recorded in the vapour phase.

(4) Microanalysis

The carbon and hydrogen content of certain monomeric precursers was determined using a Carbo Erba Elemental Analyser

1106. Samples were flash combusted to give carbon dioxide and water. These were separated and measured by quantitative gas-liquid chromatography.

(5) Determination of Molecular Weights

A Mechrolab 501 High Speed membrane osmometer equipped with a cellophane 300 membrane was used to measure number average molecular weights. All samples were dissolved in toluene to concentrations of approximately 1% w/w. A typical plot is given in Figure 2.4.

(6) Mass Spectrometry

Mass spectra of both monomers and products of degradation were recorded using an AEI MS 12 instrument with Micromass 2S8 console. The smaller Micromass QX 200 was used in the analysis of the volatile products with mass below 200.

(7) Gas Chromatography

Gas chromatograms of the products which collect on the cold finger during degradation were obtained using a Perkin-Elmer F11 Gas Chromatograph equipped with linear temperature programmer and flame ionisation detector. The column used throughout this work was a 10' x 1/4" 1% OV-1 on chromosorb.

The retention times for successively eluted compounds of equal boiling point increment increases logarithmically. This means that for similar compounds or members of a homologous series boiling over a fairly narrow range, the range of retention times will be quite large. This in turn leads to a decrease in sensitivity as the boiling point increases.

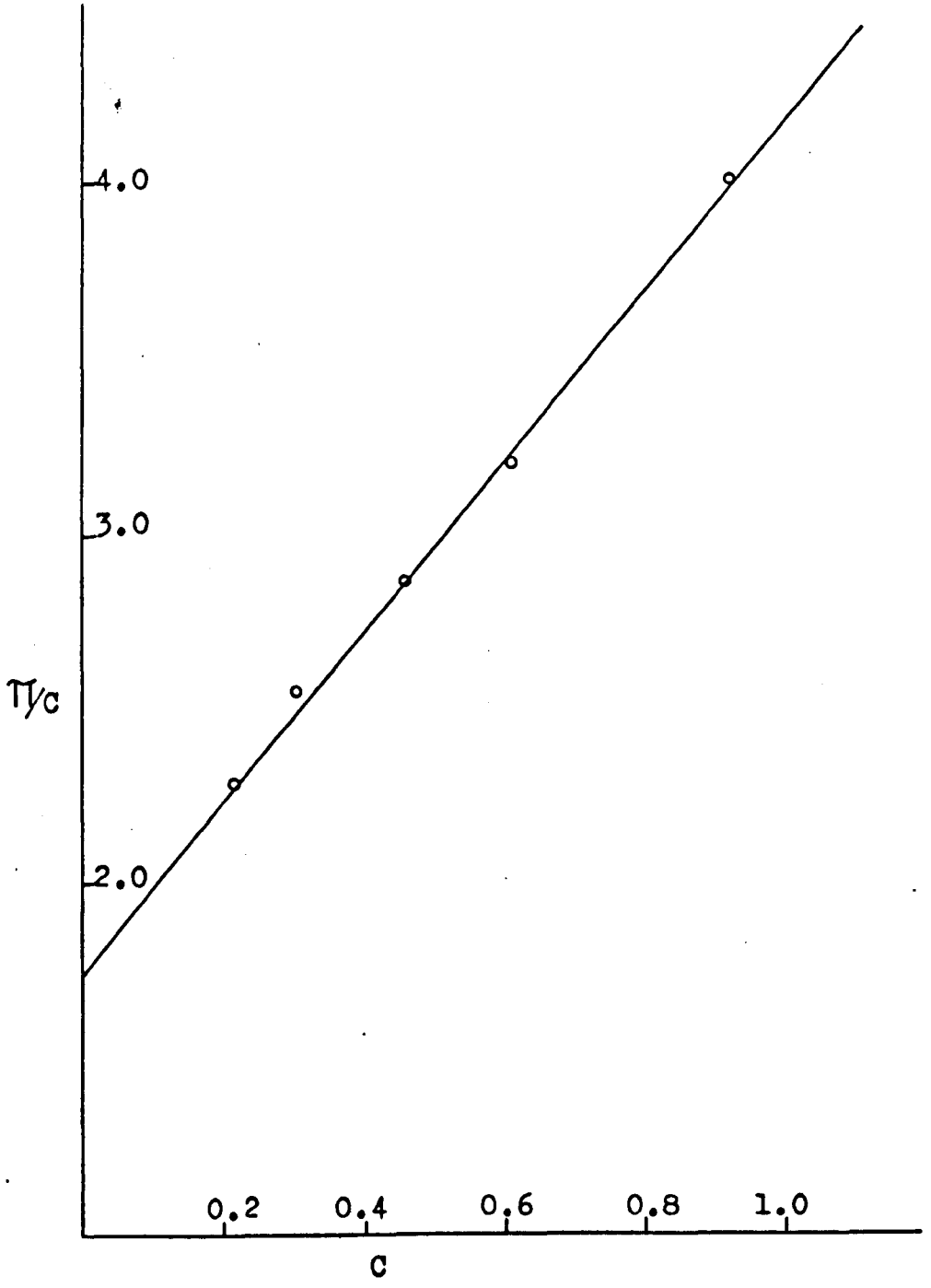


Fig. 2.4 Plot of Π/C against C for a sample of a silphenylene-siloxane polymer.
Mn=144000

Programmed temperature gas chromatography helps overcome this problem. Grant (Ref.29) found that by increasing the column temperature at a steady rate during the chromatogram, the rention time increases roughly linearly with boiling point. This relationship was verified for two homologous series; viz, aliphatic hydrocarbons and cyclic dimethylsiloxane compounds. The results are shown in Figures 2.5 and 2.6.

Many of the compounds constituting the "cold finger" fraction are similar in structure and so most effective separation is attained using temperature programming in the GC analysis.

(8) Gas Chromatography-Mass Spectrometry

Combined gas chromatography-mass spectrometry was carried out using an AEI MS 30 mass spectrometer interfaced with a Pye 104 gas chromatograph via a single stage gas jet separator. Two columns have been used, namely, 5' x 1/4" 3% OV-1 on 80-100 mesh Gas Chrom Q and 7' x 1/4" 3% Ultraphase SE 30 on chromosorb W. The carrier gas was helium and temperature programming was used in each case. Mass spectra were obtained with an electron energy of 70 eV.

(9) Sol Gel Analysis

A weighed sample of the polymer residue in a ground-glass stoppered bottle was covered with a 10 ml. aliquot of analar toluene. After 24 hours the toluene was replaced with a fresh 10 ml. aliquot. This procedure was carried out five times in total, the temperature being maintained at 25°C throughout. The final gel was dried in a

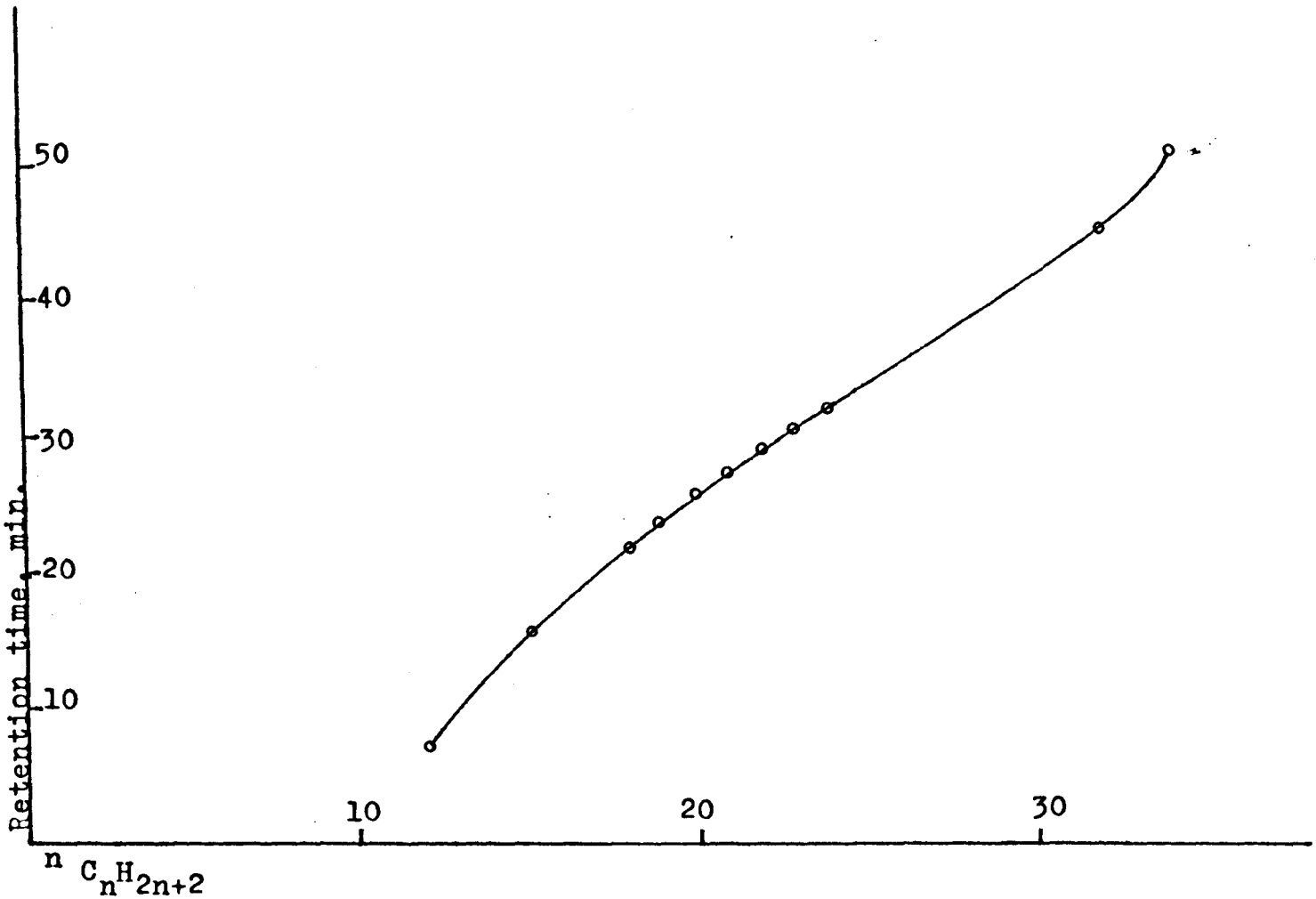


Fig. 2.5 Plot of retention time against n for the homologous series of aliphatic hydrocarbons, C_nH_{2n+2}. Programme, $5^{o}min^{-1}$ from 50^{o} to 270^{o} and thereafter held at 270^{o}.

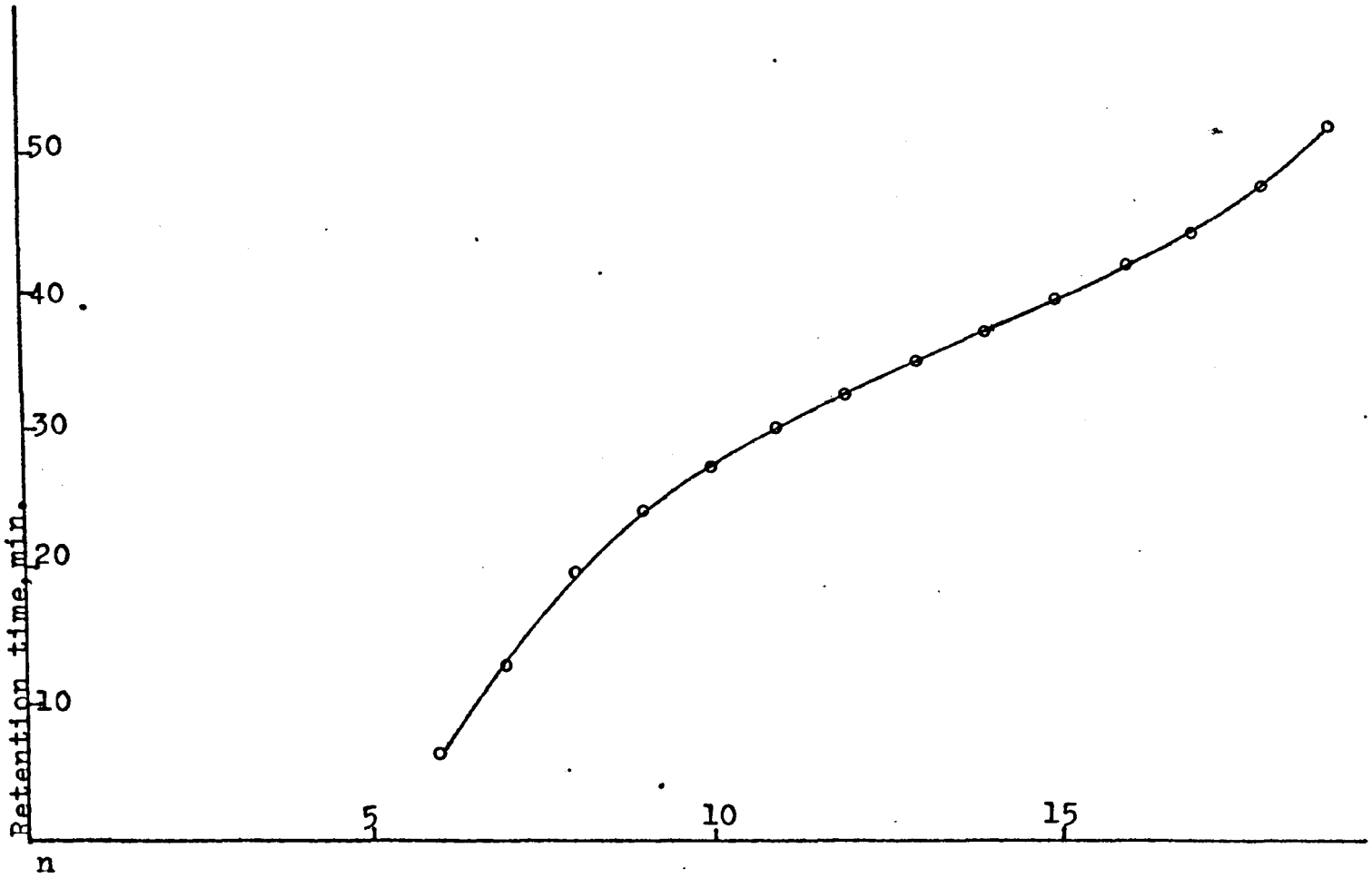


Fig. 2.6 Plot of retention time against n for the series of cyclic dimethylsiloxane oligomers, D_n. Programme, $5^{o}min^{-1}$ from 50^{o} to 270^{o} and thereafter held at 270^{o}.

vacuum oven at ambient temperature for 72 hours before taking the final dry weight of the gel fraction.

The rates of both chain scission and crosslinking can be obtained from measurement of the sol fraction via the Charlesby-Pinner equation (Ref. 28).

$$S + \sqrt{S} = {}^{p_o}/_{q_o} + \frac{1}{q_o u t}$$

in which S is the soluble fraction after time t, p_o is the number of scissions per monomeric unit per unit of time, q_o is the number of crosslinked units per monomeric unit per unit of time and u is the number average degree of polymerisation of the starting material. Thus p_o and q_o /2 are the rates of scission and crosslinking per monomeric unit.

CHAPTER 3

SYNTHESIS AND CHARACTERISATION

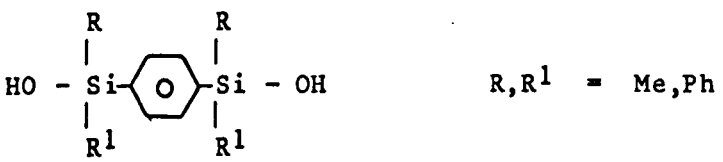
3.1. Introduction

Many cyclic dialkyl, alkylaryl or diaryl siloxanes may be polymerized under the influence of a suitable acidic or basic catalyst to yield linear siloxane polymers. Thus in the preparation of TMPS, a cyclic oligomer of tetramethyl-p-silphenylenesiloxane would appear to be a convenient starting unit to which existing techniques may be applied. Merker and Scott (Ref. 20) reported that although these cyclic compounds could be polymerized readily to form a tough, fibre forming polymer, the difficulties encountered in obtaining the cyclic monomers in high yield suggested that an alternative approach may be more satisfactory. They prepared the linear polymer via a dilute solution intermolecular hydroxyl condensation reaction of p-phenylenebis (dimethylsilanol). Since this monomer is more readily prepared in high yield, this method would seem to be more attractive.

Block copolymers of TMPS and DMS were prepared by Merker, Scott and Haberland (Ref. 30) in a condensation reaction between hydroxy end-grouped dimethylpolysiloxanes and p-phenylenebis (dimethylsilanol). This silanol condensation was catalysed by one of two non-equilibrating

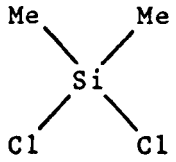
catalysts, namely n-hexylamine 2-ethylhexoate and tetramethylguanidine di-2-ethylhexoate. These catalysts are incapable of rearranging the siloxane bonds and so do not affect the length of the starting hydroxy ended polydimethylsiloxanes. When a catalyst such as potassium dimethylsilanolate (Ref. 30) or potassium hydroxide (Ref. 25) is employed then a siloxane monomer such as octamethylcyclotetrasiloxane may be used with the p-phenylenebis (dimethylsilanol). This will result in the formation of a random copolymer.

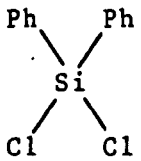
Arylenedisilanols, represented by the general structure

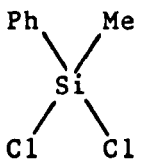


are frequently obtained by use of an "in situ" Grignard technique (Ref. 20,25,31). Arylenedisilane derivatives are formed in a single synthesis step where the difunctional Grignard reagent from magnesium and p-dibromobenzene is formed in the presence of a diorganosilane compound. Although in much of the literature this compound is the diorganochlorsilane (Ref. 32,33) the method has been shown to be effective with a diorganodichlorosilane (Ref. 34), a diorganochloroalkoxysilane (Ref. 31) or a diorganodialkoxysilane (Ref.35). Hydrolysis of the arylenedisilane derivative gives the required diol.

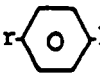
3.2. Sources of Reagents.

dichlorodimethylsilane  was obtained from Peninsular Chemical Research (P.C.R.) Inc., Florida, U.S.A. This is repackaged Dow Corning Z-129 silane.

dichlorodiphenylsilane  was obtained from Aldrich Chemical Company Inc. (U.S.A.).

dichloromethylphenylsilane  was obtained from Aldrich Chemical Company Inc. (U.S.A.).

diethoxydimethylsilane  was obtained from Aldrich Chemical Company Inc. (U.S.A.) Specification 99%.

p-dibromobenzene  was obtained from two sources

(a) The British Drug Houses Ltd. (London),

(b) Aldrich Chemical Company Ltd. (England). Specification 97%.

magnesium turnings were obtained from The British Drug Houses Ltd. (England). Minimum assay 99.7% Mg.

tetramethylammonium hydroxide $(CH_3)_4NOH$ was obtained as a 25% aqueous solution from Hopkin and Williams Ltd.

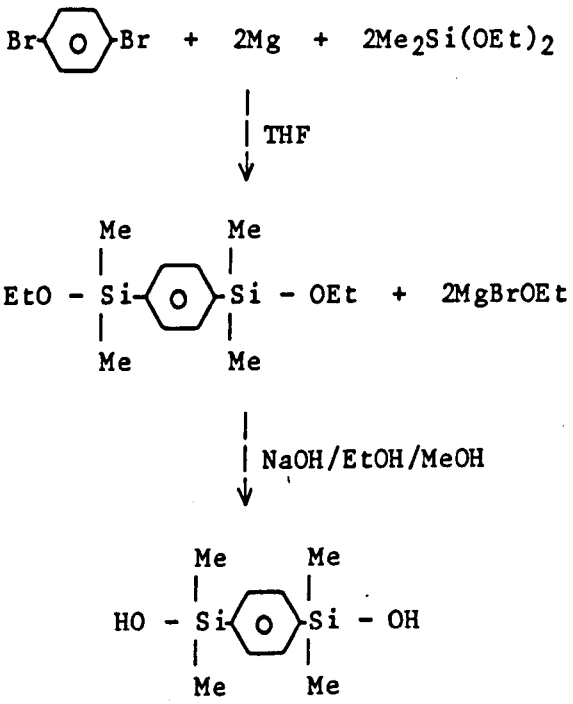
tetramethylguanidine $Me_2N - \overset{\overset{NH}{\|}}{C} - NMe_2$ was obtained from the Alfred Bader Library of Rare Chemicals, a division of Aldrich Chemical Company Inc. (U.S.A.).

2-ethylhexanoic acid $CH_3(CH_2)_4\,\overset{\overset{Et}{|}}{CH}.CO_2H$ was obtained from Aldrich Chemical Company Inc. (U.S.A.). Specification 99%.

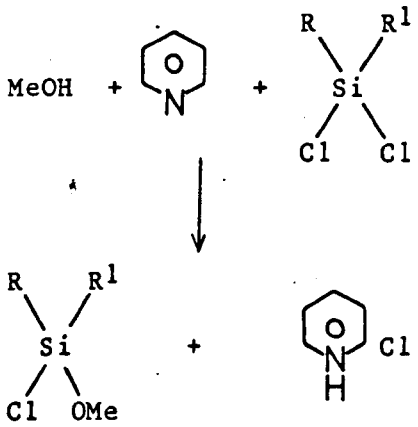
Other reagents and solvents used in this project were in all cases of Analar grade.

3.3. Preparation of Monomers

A brief outline of the synthesis of p-phenylenebis (dimethylsilanol) is given below.



The corresponding methylphenyl and diphenyl substituted diols were prepared from the diorganochloromethoxysilane in a reaction similar to that outlined above. The chloromethoxy derivative was prepared from the diorganodichlorosilane. This can be summarised as follows:-



1. p-phenylenebis (dimethylsilanol)

Magnesium turnings (0.45g atoms:10.9g) were placed in a flask equipped with dropping funnel, reflux condenser and stirrer, and covered with freshly distilled THF (40 ml). A solution of p-dibromobenzene (0.2 mole: 47.2g) and diethoxydimethylsilane (0.45 mole: 77.2 ml) in THF (100 ml) was added dropwise over 1.5 - 2.0 hours with rapid stirring. After refluxing for a further 3 hours the mixture was cooled and treated with petroleum ether (100 ml) to precipitate the magnesium salts. Filtration of the mixture followed by fractional distillation under reduced pressure gave the p-phenylenebis (dimethylethoxysilane) (bp 119-120°;3.6mm).

A solution of p-phenylenebis (dimethylethoxysilane) (0.055 mole:15.5g) in ethanol (60 ml) was added dropwise over 0.5 hour to a stirred solution of sodium hydroxide (0.3 mole: 12g) in water (7.5 ml) and methanol (60 ml). A further addition of sodium hydroxide (0.3 mole; 12g) in water (33 ml) was made over a period of 10 minutes. After stirring the mixture for a further hour, it was poured into water (150 ml) containing ice (400 g) and potassium dihydrogen phosphate

(0.65 mole:88g). Filtration and recrystallisation from toluene gave the pure diol as was verified from the melting point (135°), infrared and n.m.r. spectra and microanalysis.

2. p-phenylenebis (methylphenylsilanol)

A mixture of anhydrous methanol (0.55 mole: 22.3 ml) and pyridine (0.55 mole: 44.5 ml) was added dropwise to methylphenyldichlorosilane (0.55 mole: 89.4 ml) while stirring constantly. After stirring for a further 30 minutes the mixture was filtered and fractionally distilled. Chloromethylphenylsilane boiled at 93-96° (18 mm).

Subsequent preparation of the silanediol via p-phenylenebis (methylphenylmethoxysilane) was carried out as described in the p-phenylenebis (dimethylsilanol) preparation.

3. p-phenylenebis (diphenylsilanol)

Starting from diphenyldichlorosilane, the process followed was that in 3.3.2. Diphenylchloromethoxysilane boiled at 186°(17mm).

4. Tetramethyldisiloxanediol

Ammonium carbonate (1.40 mole: 220g) and distilled water (820ml) were placed in a flask equipped with dropping funnel, stirrer and thermometer. Dichlorodimethylsilane (1.07 mole: 130 ml) was added dropwise over a period of 2.5 hours during which time the temperature was maintained at 0°. The reaction mixture was saturated with sodium chloride, the excess being removed by filtration. Storage of the filtrate at -5° for 48 hours allowed the product to crystallise. Pure tetramethyldisiloxanediol was obtained by

recrystallisation from petroleum ether (40°- 60°) and characterised from the melting point (68°), infrared and n.m.r. spectra.

5. Octamethylcyclotetrasiloxane

A flask equipped with stirrer, dropping funnel and thermometer containing distilled water (750 ml) was immersed in an ice/water bath. While maintaining the temperature below 20° dichlorodimethylsilane (2.06 mole: 250 ml) in anhydrous diethylether (250 ml) was added dropwise to the flask. Since this reaction is exothermic, the limit of 20° maximum in temperature controls the rate of addition.

The ethereal layer containing the hydrolysis products was separated from the excess water, washed repeatedly with a dilute sodium bicarbonate solution, to remove HCl, and finally with distilled water. Anhydrous magnesium sulphate removed excess moisture. Filtration, followed by removal of the solvent under reduced pressure by rotary evaporation, left an oily substance. Distillation of the oil under reduced pressure (25 mm) separated the low molecular weight cyclic siloxanes from the non-volatile products of hydrolysis. The oil was redistilled several times to give progressively purer tetramer (bp 175°; 760mm). Infrared and mass spectroscopy were used to characterise the product and the purity was checked using gas chromatography.

3.4. Preparation of Catalyst

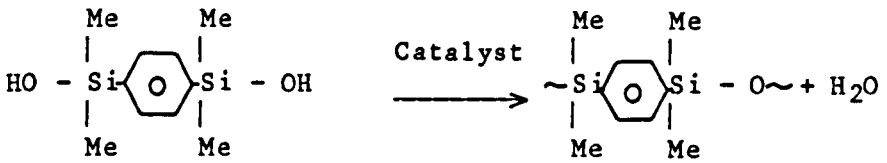
1. tetramethylguanidine di-2-ethylhexoate

This nonequilibrating catalyst was prepared by simply mixing 2-ethylhexanoic acid (0.01 mole: 1.44 g) with

tetramethylguanidine (0.05 mole: 0.57 g)

3.5. Preparation of TMPS

A schematic outline for the preparation of the TMPS homopolymer is given below.



1. TMAH Catalysed Polymerization

(a) A dilute solution polymerization of p-phenylenebis (dimethylsilanol) in toluene catalysed by tetramethylammonium hydroxide (TMAH), was attempted. The reaction mixture, which contained 50% by weight of monomer and 0.1% by weight of catalyst was placed in a r.b. flask equipped with reflux condenser and azeotropic trap. After 6 hours reflux an infrared spectrum of the reaction mixture showed the absorption band due to the Si-O-Si group to be weak while that due to the Si-OH group was still strong.

(b) Polymerization of the diol catalysed by TMAH was repeated with two modifications to the above process. The catalyst concentration was increased to 0.3% by weight of the final reaction mixture and the time of reflux was extended to 33 hours. At the end of the reflux period the toluene was removed by distillation and residual catalyst was destroyed by heating the sample to 135° for 20 minutes. The polymer was purified by repeatedly dissolving in toluene and reprecipitating from methanol. When no change was observed in TG traces from the products obtained from two successive

isolations purification was considered complete.

2. KOH catalysed polymerization

p-phenylenebis (dimethylsilanol) was dissolved in an equal weight of toluene and KOH (0.1 wt -%) was added as a 1% aqueous solution to catalyse the condensation. After thoroughly mixing the contents, the flask was placed in a thermostat and a continuous stream of dry oxygen-free nitrogen blown through. The temperature of the reaction mixture was increased to 150°, during which the toluene was removed, and thus maintained for 6 hours. The resulting polymer was purified as described in 3.5.1 (b).

3. TMG catalysed polymerization

Tetramethylguanidine di-2-ethylhexoate (TMG) was used to catalyse a solution polymerization of p-phenylenebis (dimethylsilanol) in toluene. The final reaction mixture contained 66% by weight monomer and 0.5% by weight catalyst. The solution was refluxed for 9 hours during which time the water was removed azeotropically as it was formed. Purification of the final polymer has been described in 3.5.1 (b).

3.6 Characterisation of TMPS

1. Infrared analysis

The infrared spectrum of TMPS is given in Figure 3.1. Table 3.1 contains assignments of the major absorptions. The presence of the broad absorption band at 1100 - 1000 cm^{-1} due to the Si-O-Si group combined with the absence of the bands at 3400 - 3200 and 840 cm^{-1}

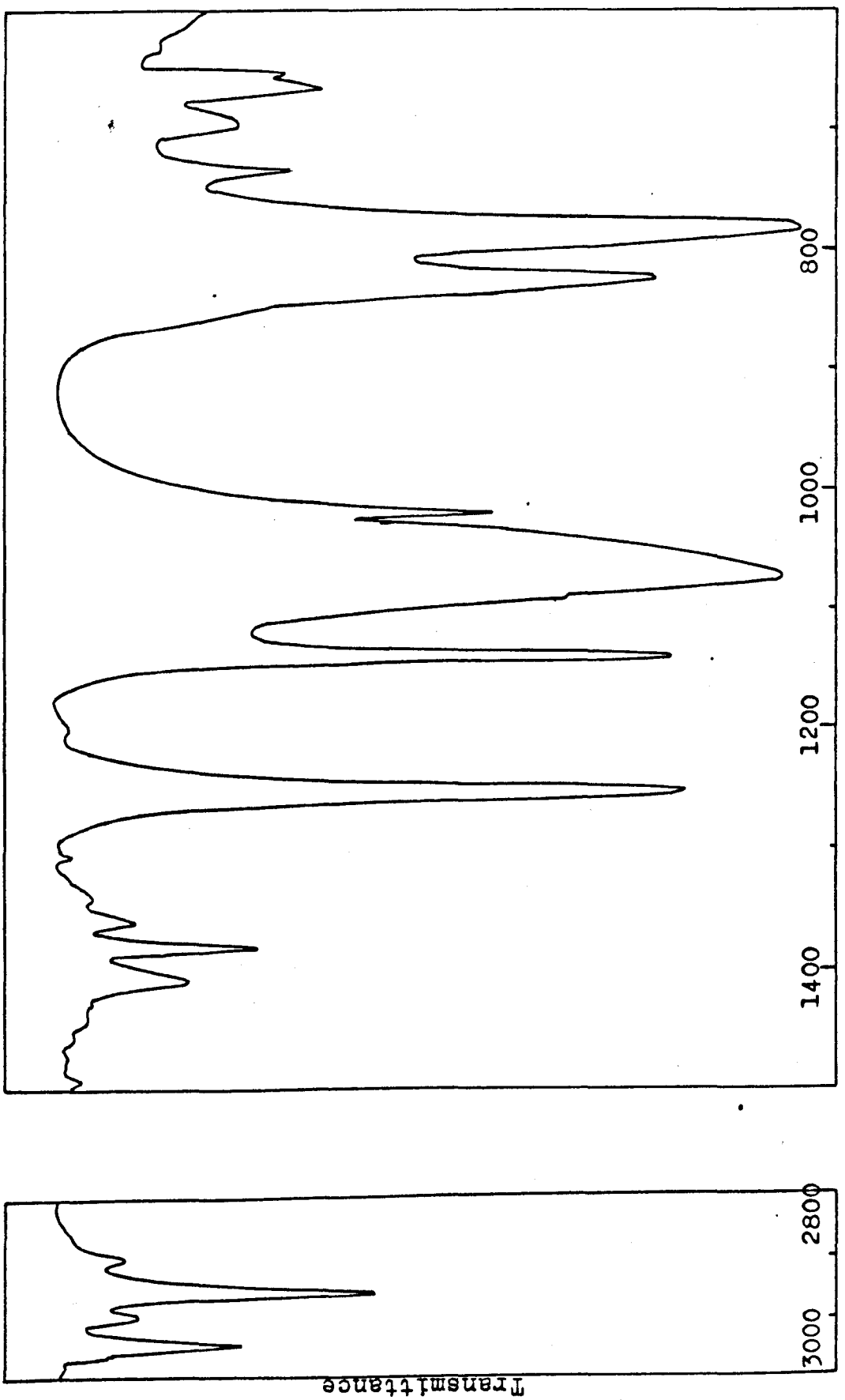


Fig. 3.1 Infrared spectrum of TMPS.

characterising the SiOH group indicate the success of the intermolecular condensation of the hydroxyl groups to form the siloxane linkage.

2. n.m.r. spectroscopy

The proton n.m.r. spectrum of TMPS is illustrated in Figure 3.2. The singlet at τ= 9.48 ppm is attributed to the protons of the methyl substituent groups while the p-phenylene group gives rise to the singlet at τ = 2.34 ppm.

Group	Band (cm^{-1})	Remarks
Si-Phenyl	3100 - 3000	At least 5 sharp bands due to aromatic C-H stretching.
	1440	Aromatic C-C ring stretching vibration giving a sharp absorption. This is a very useful band for detecting phenyl on silicon.
	1130	Intense band from a planar ring vibration with some Si-C stretch character.
	750 - 690	Out of plane hydrogen vibrations of the phenyl group.
Si-Methyl	2960 - 2850	C-H stretching vibrations
	1380	Asymmetric Si-Me deformation.
	1250	Symmetric Si-Me deformation.
	830 - 770	Si-C stretching vibrations. Two bands present indicate the presence of dimethyl-substituted silicon.
Si-O-Si	1100 - 1000	Two or more absorption maxima due to the asymmetric Si-O-Si stretch.

TABLE 3.1

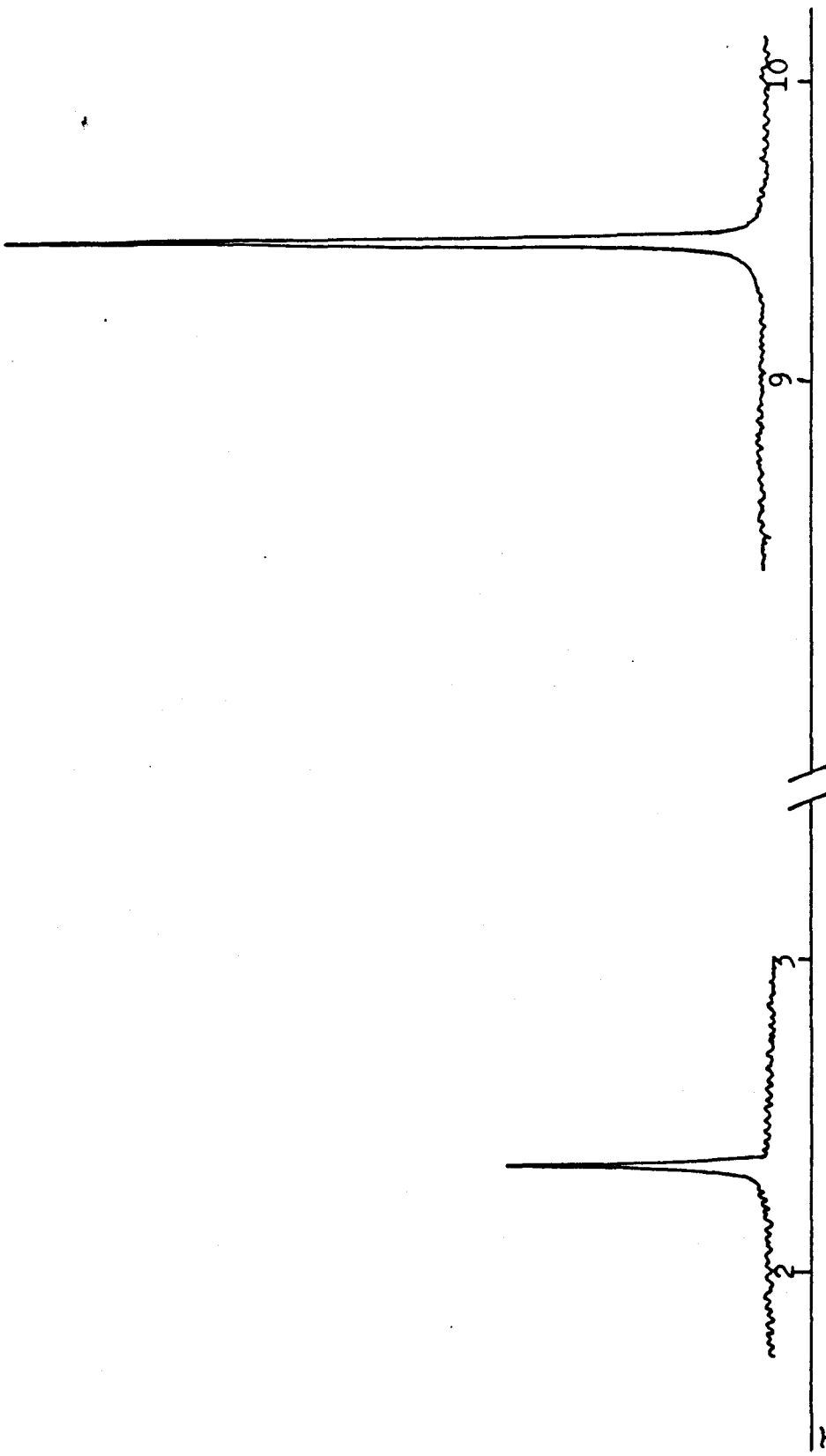


Fig. 3.2 n.m.r. spectrum of TMPS.

3. Membrane osmometry

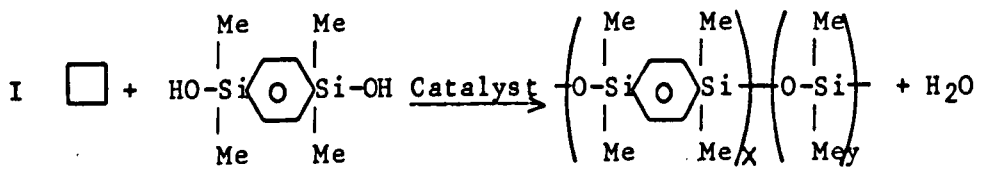
Number average molecular weights, Mn, were measured and the results are recorded in Table 3.2.

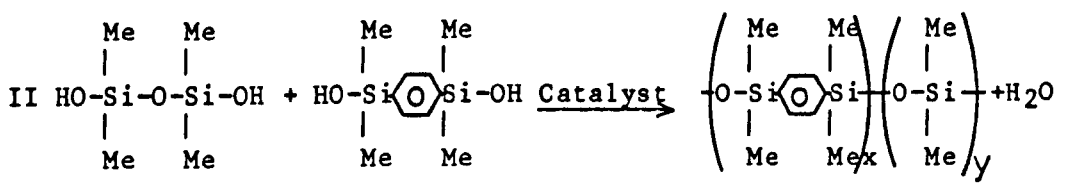
Catalyst Used	Concentration Wt. %	Polymerization Time (Hours)	Mn
TMAH	0.1	6	-
TMAH	0.3	33	27000
KOH	0.1	6	21500
TMG	0.5	9	123000

TABLE 3.2

3.7 Preparation of the TMPS/DMS Copolymers

Copolymers consisting of TMPS and DMS monomer units were prepared by the reaction of p-phenylenebis (dimethylsilanol) with either octamethylcyclotetrasiloxane or tetramethyldisiloxanediol. These processes are outlined in schemes I and II respectively.





The polymer synthesis procedures were as follows. Variations in experimental detail and the quantities of the respective monomers used are summarised in Table 3.3.

1. TMAH catalysed polymerization

The two monomers octamethylcyclotetrasiloxane and

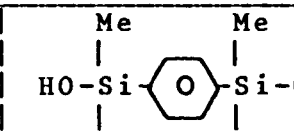
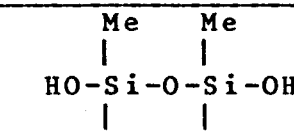
Polymer	 Mole %	 Mole %	Mole %	Catalyst	Concentration of Catalyst Wt-%	Polymerisation Time (Hours)
-	50.0		50.0	TMAH	0.6	6
A	17.4	82.6		TMG	0.5	16 *
B	33.3	66.7		TMG	0.5	9
C	60.9	39.1		TMG	0.5	9
D	50.0		50.0	KOH	0.06	6
E	80.0		20.0	KOH	0.1	6
F	88.9		11.1	KOH	0.1	6

TABLE 3.3

* A was heated under vacuum at 100° for 16 hours after isolation

p-phenylenebis (dimethylsilanol) dissolved in toluene to give a 64 wt -% solution were placed in a flask equipped with reflux condenser and azeotrope trap. TMAH catalyst was added and the reaction mixture refluxed for 6 hours. Residual catalyst was destroyed by raising the temperature of the reaction mixture to 150° for 20 minutes. Repeated dissolution in toluene and reprecipitation from methanol gave the pure polymer.

2. KOH catalysed polymerization

The cyclic siloxane monomer and the arylenedisilanol were dissolved in toluene to a concentration of 66 wt -%. Catalyst was added as a 1% aqueous solution and the flask contents were mixed thoroughly. The toluene was removed when the temperature of the reaction mixture was raised to 150° in a dynamic atmosphere of oxygen-free nitrogen.
After polymerizing for 6 hours at 150° the polymer was purified as in 3.5.1(b).

3. TMG catalysed polymerization

A toluene solution containing 66 wt -% monomer and TMG catalyst was placed in a flask eqipped with reflux condenser and toluene filled azeotrop trap. In this case the monomers used were tetramethyldisiloxanediol and p-phenylenebis (dimethylsilanol). After refluxing for a given period of time, the copolymer was isolated by precipitation from methanol. Low molecular weight impurities and any residual catalyst were removed by repeated dissolution in toluene and reprecipitation from methanol.

3.8. Characterisation of the TMPS/DMS copolymers

1. Infrared analysis

The same absorption bands are present in all the infrared spectra of the complete series of copolymers. Figure 3.4 illustrates that of TMPS/DMS C as being typical. Assignments of the major absorptions are given in Table 3.1. As in the formation of the homopolymer, the disappearance of the bands due to the SiOH group at 3400-3200 and 840 cm^{-1} implies formation of the polymer.

2. n.m.r. spectroscopy

The chemical shift of the Si-Me group when situated between two oxygen atoms is sufficiently different from that between an oxygen and a p-phenylene group for both resonances to be resolved. This is illustrated in Figure 3.5. The bulk composition of each copolymer was determined from the integral values of the different resonances. These results are recorded in Table 3.4.

3. Membrane osmometry

The number average molecular weight of each polymer was measured and the results recorded in Table 3.4.

3.9. Preparation of MPPS

Poly(methylphenyl-p-silphenylenesiloxane), MPPS was prepared by refluxing 33 wt-% of p-phenylenebis (methylphenylsilanol) in toluene with 0.5 wt-% TMG catalyst. Water was removed azeotropically as formed during the 16 hour reflux. Purification was carried out as previously described.

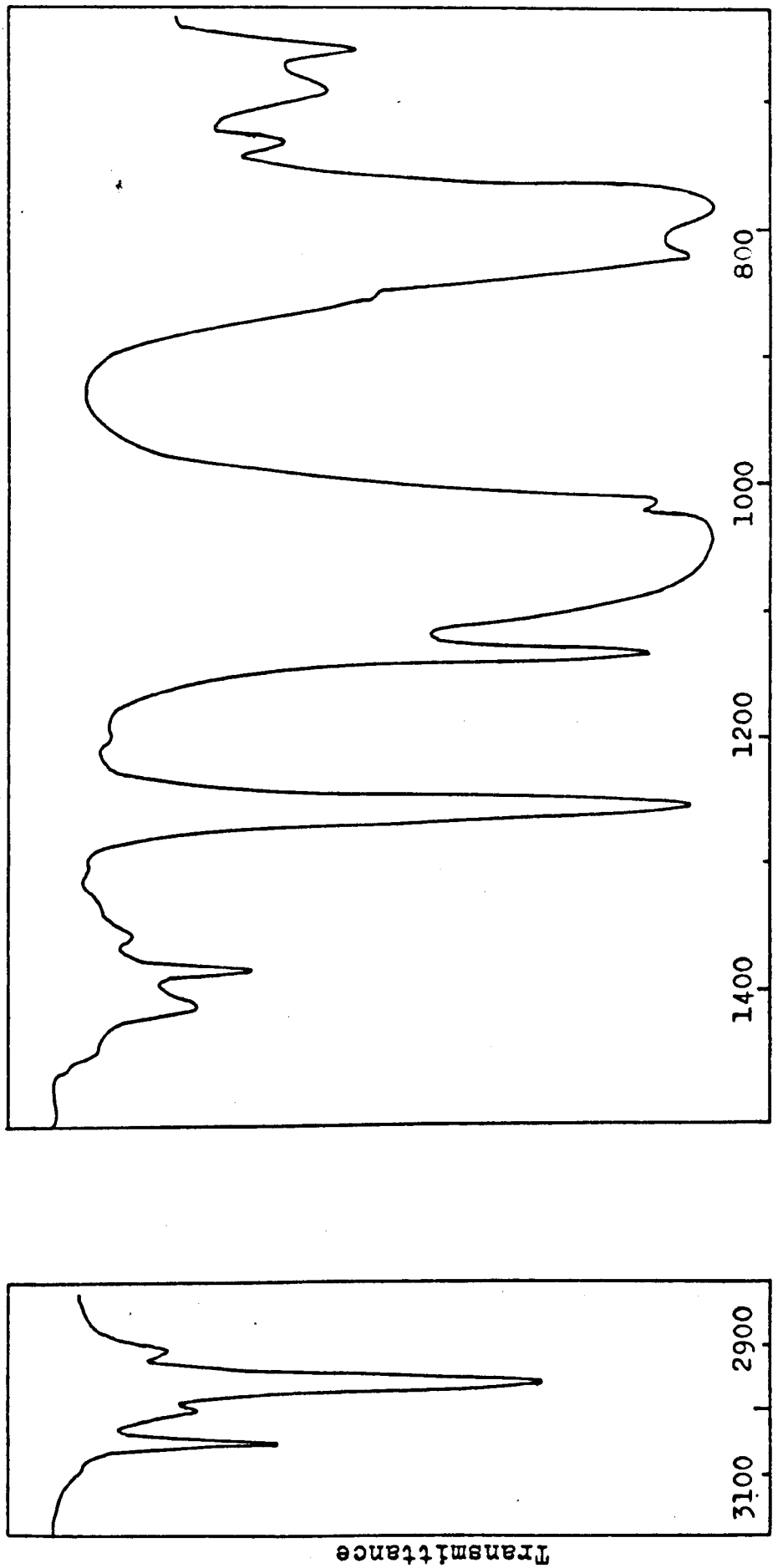


Fig. 3.4 Infrared spectrum of TMPS/DMS C.

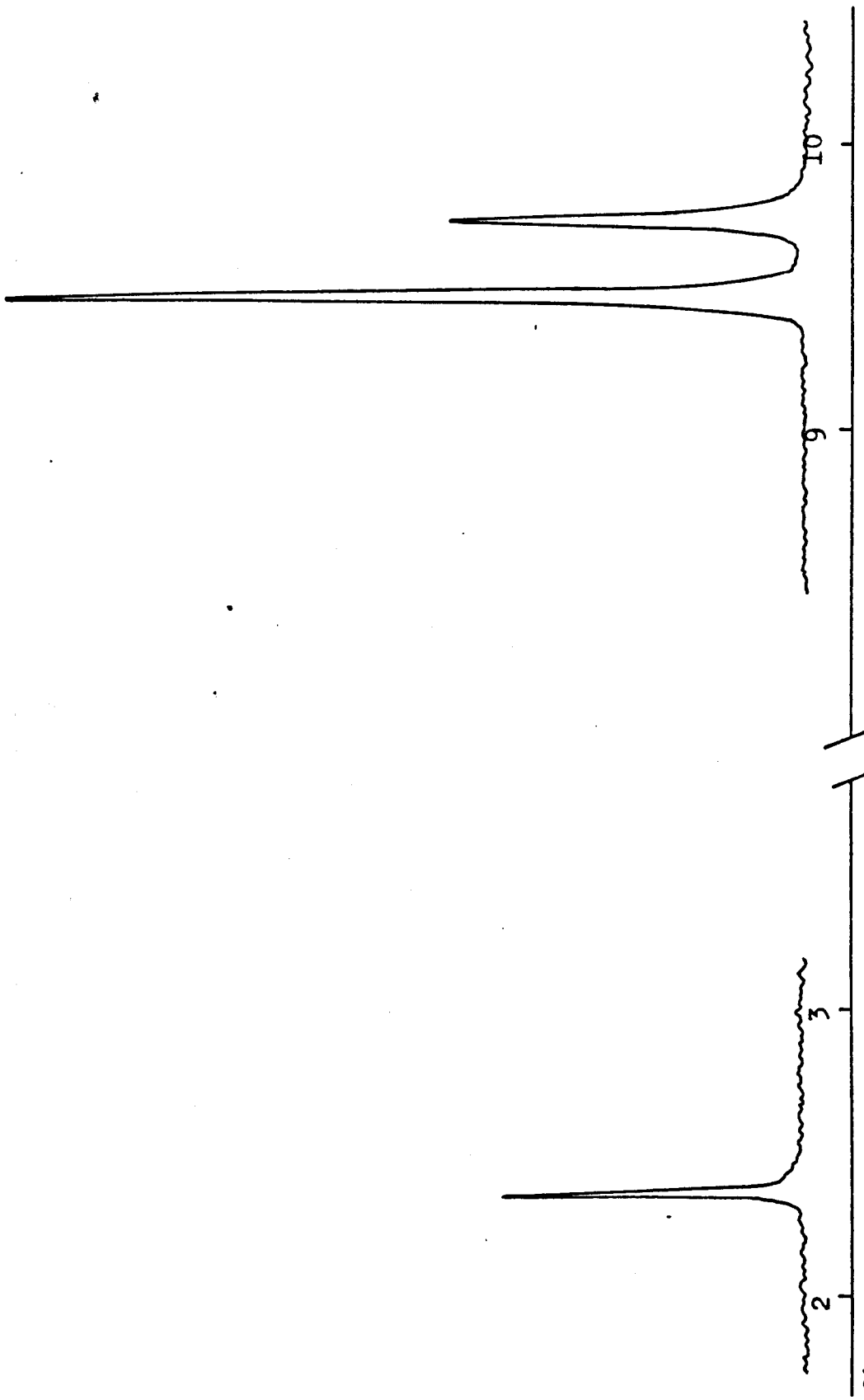


Fig. 3.5 n.m.r. spectrum of TMPS/DMS C.

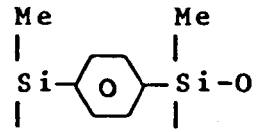
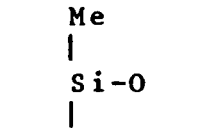
Polymer	Copolymer Composition		Mn
	 Mole %	 Mole %	
A	15.0	85.0	52000
B	23.4	76.6	72400
C	46.7	53.3	52700
D	52.9	47.1	110000
E	80.6	19.4	33100
F	89.3	10.7	26900

TABLE 3.4

3.10 Characterisation of MPPS

1. Spectroscopy

Infrared and n.m.r. spectra of the polymer were recorded. These are illustrated in Figures 3.6 and 3.7. Assignments of the major infrared absorptions are given in Table 3.5.

2. Membrane osmometry

The number average molecular weight was measured in toluene and found to be 35200.

3.11 Preparation of TPPS

1. TMG catalysed polymerization.

Starting with p-phenylenebis(diphenylsilanol) the preparation was carried out in a manner analogous to that of MPPS.

2. KOH catalysed polymerization.

The technique adopted here was described in 3.5 2. The sample was heated over a period of 12 hours.

3.12 Characterisation of TPPS.

The infrared and n.m.r. spectra are given in Figures 3.8 and 3.9. Assignments of the major absorptions are listed in Table 3.5. The Mn was not high enough to be measured by membrane osmometry.

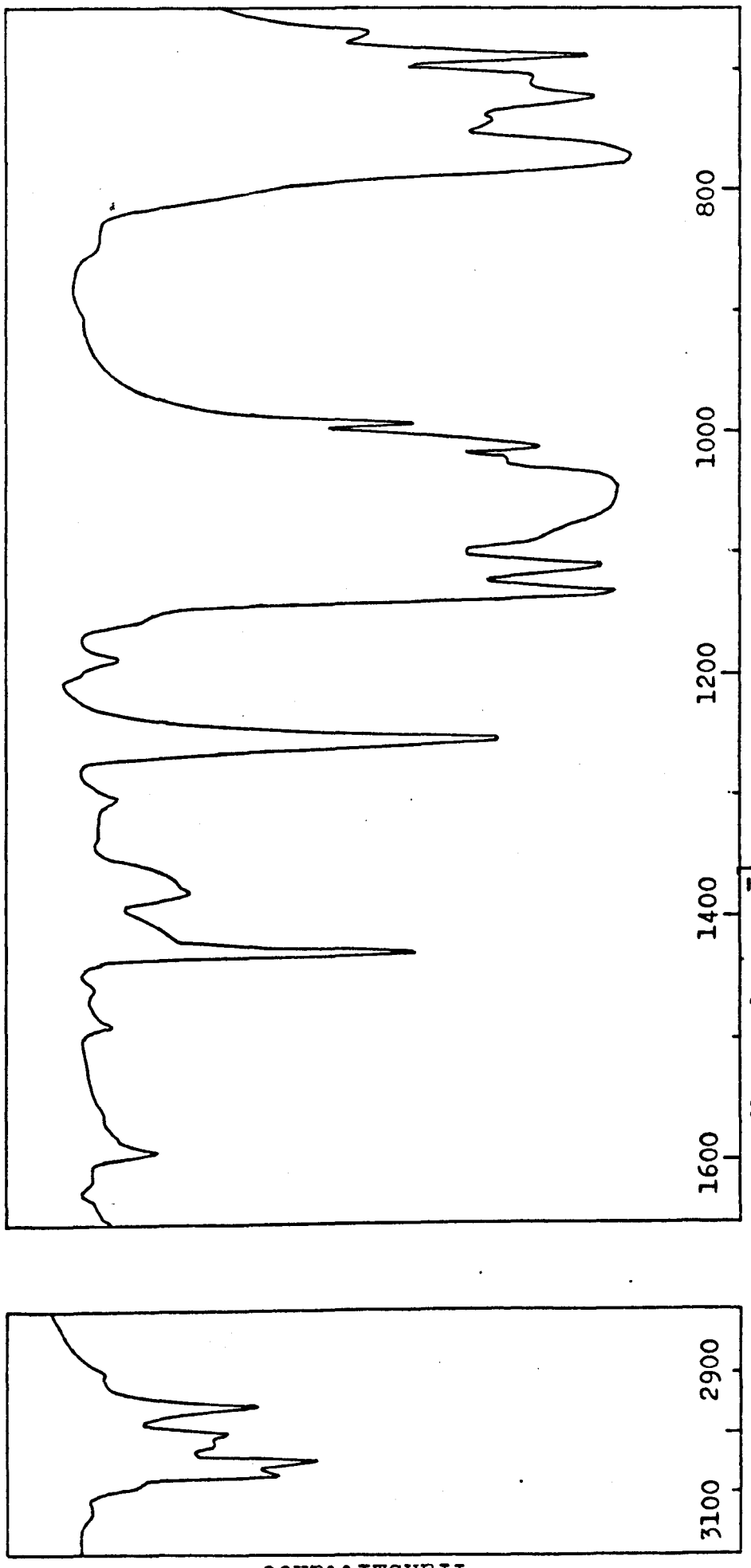


Fig. 3.6 Infrared spectrum of MPPS.

Group	Band (cm^{-1})	Remarks
Si-phenyl	3100 - 3000	At least 5 bands due to the aromatic C-H stretching.
	1590 & 1490	Phenyl ring absorptions.
	1430	Aromatic C-C ring stretching vibration giving a sharp absorption.
	1140 - 1120	Intense band from a planar ring vibration with some Si-C stretch character. This appears as a doublet when two phenyl rings are attached to the silicon.
	1020 & 1000	Two weak sharp bands.
	750 - 690	Out of plane hydrogen vibrations of the phenyl group. The two bands at 720 and 690 cm^{-1} arise from monosubstituted aromatic rings.
	550 - 520	Doublet due to the aromatic ring.
Si-methyl	2960 - 2850	C-H stretching vibrations.
	1380	Asymetric Si-Me deformation.
	1250	Symetric Si-Me deformation.
	780	Si-C stretching vibration. This is a single band for monomethyl-substituted silicon.
Si-O-Si	1100 - 1000	Two or more absorption maxima due to the asymetric Si-O-Si stretch.

TABLE 3.5

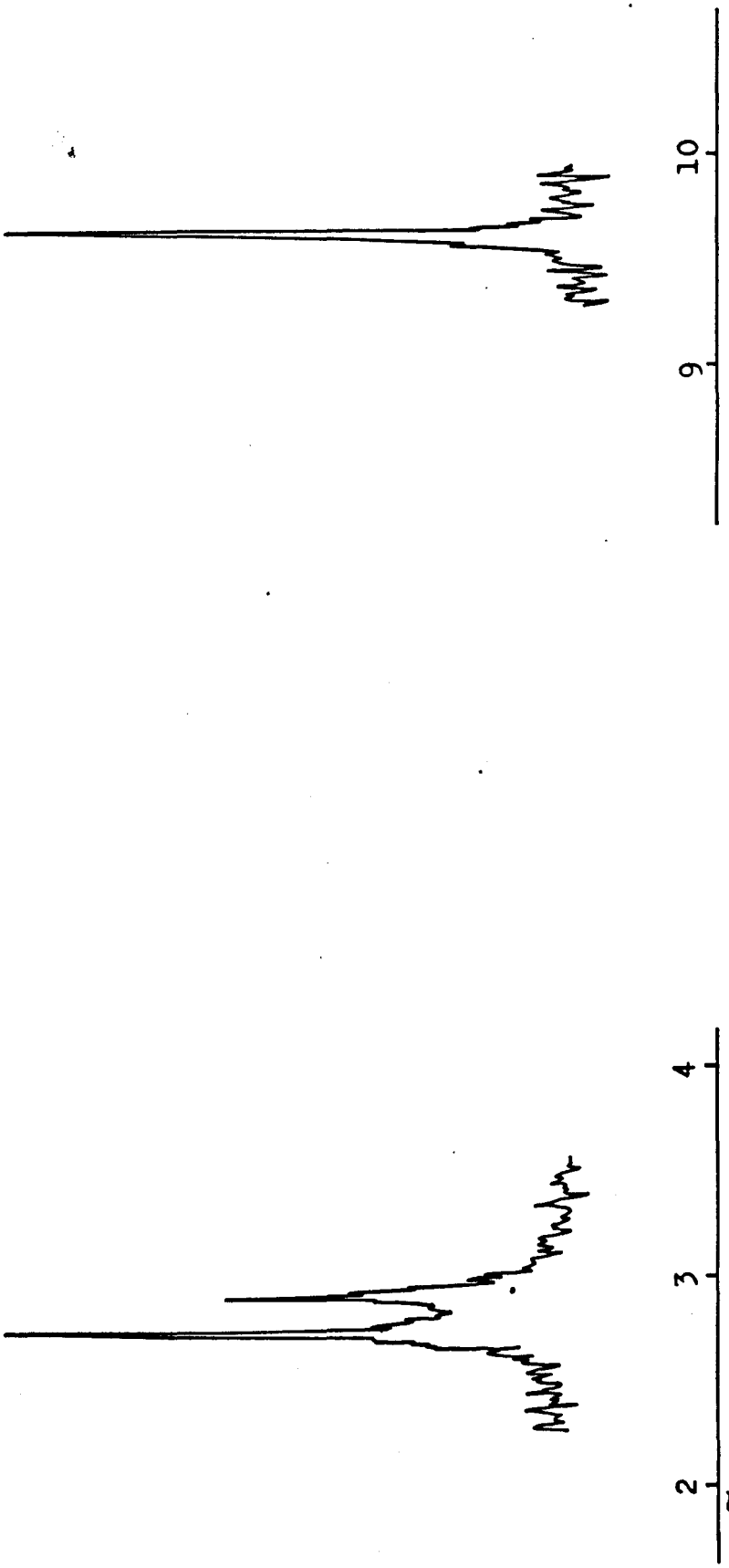


Fig. 3.7 n.m.r. spectrum of MPPS.

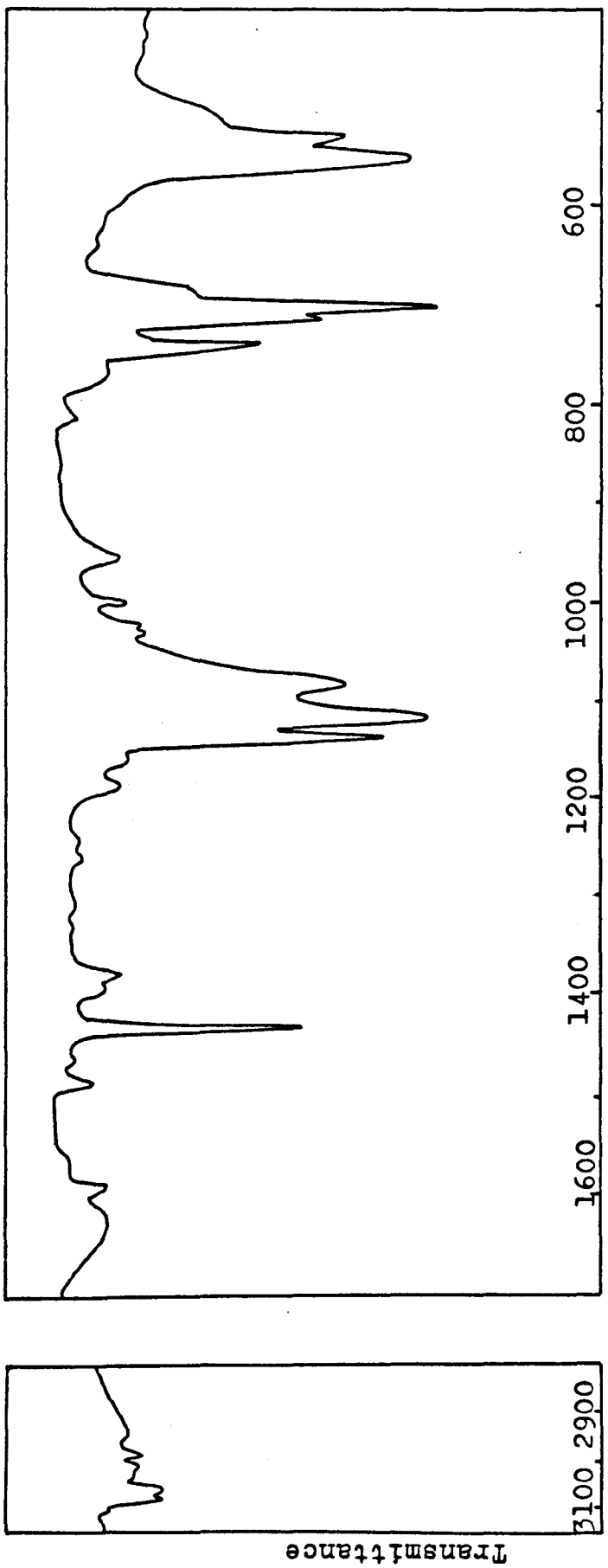


Fig. 3.8 Infrared spectrum of TPPS.

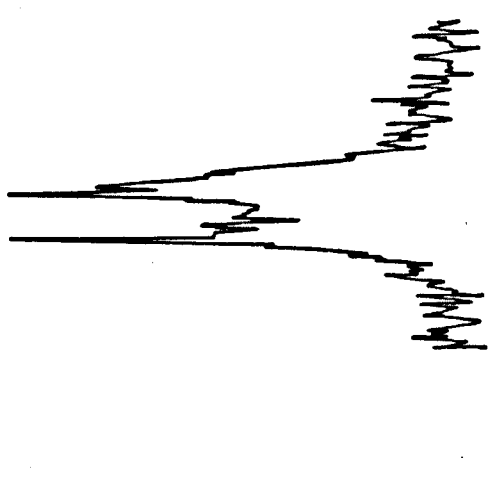


Fig. 3.9 n.m.r. spectrum of TPPS.

3.13 Discussion

Polydimethylsiloxanes are obtained frequently from the anionic polymerization of cyclic siloxanes using basic catalysts such as potassium dimethylsilanolate, KOH or TMAH. One of the problems associated with the use of a catalyst of this type is the adverse effect of any residual catalyst in the final polymer on its overall thermal stability. Several workers (Ref 36,37,38) have demonstrated this fact and much work has been done to find an efficient way of removing the catalyst from the final siloxane polymer. Three well established methods for making the catalyst inactive are:-

(a) extraction of the catalyst with water,

(b) neutralising the residual catalyst,

(c) use of a thermally labile catalyst.

In practice neutralisation or extraction of a species present in concentrations as low was 0.1% in a medium of high viscosity is difficult. A catalyst which decomposes to inactive products at temperatures where the polymer itself is thermally stable would appear to be a more satisfactory solution.

In the initial attempts to prepare the silphenylene-siloxane polymers the catalyst selected was TMAH. This catalyst decomposes rapidly at 130° forming trimethylamine and methanol.

$$(CH_3)_4NOH \longrightarrow (CH_3)_3N + CH_3OH$$

Macfarlane (Ref 39) demonstrated by way of thermogravimetry

that neither the residual catalyst nor its breakdown products affect the thermal stability of siloxane polymers. Unfortunately the TMAH catalysed polymerizations of p-phenylenebis(dimethylsilanol) did not prove to be too successful. After several hours reflux it was evident from the infrared spectrum that the extent of polymerization was small. Increasing the catalyst concentration and the reflux time met with little success.

Replacement of TMAH by KOH allows the polymerization to be carried out at an increased temperature while using a similar type of catalyst. After 6 hours at 150° a high molecular weight polymer was formed. When Andrianov (Ref 25) used this catalyst to prepare the TMPS/DMS copolymers and the TMPS homopolymer he rendered it inactive by neutralising with acetic acid. In this project purification was carried out by repeatedly dissolving the polymer in toluene and reprecipitating from methanol. A polymer was considered to be pure when samples from successive isolations gave similar TG traces.

High molecular weight polymers were formed in the TMG catalysed polymerizations. TMG catalyses the condensation between two silanol groups but has no effect on the siloxane bonds in the growing polymer. This inability to rearrange siloxane bonds was demonstrated by Merker, Scott and Haberland (Ref 30). Therefore efficient removal of TMG from the final polymer is not so critical as in the case of the KOH catalysed

polymerization.

It would appear that TMPS and the TMPS/DMS copolymers may be prepared using either the basic catalyst, KOH, or the non equilibrating catalyst, TMG. The deleterious effects of residual KOH on the thermal stability of a siloxane polymer has led to a slight preference being given to TMG in this work. Therefore when MPPS and TPPS were prepared this was the catalyst chosen.

The results from both molecular weight measurement and spectroscopic analysis indicate the successful formation of MPPS. However polymerization of p-phenylenebis(diphenylsilanol) was not so satisfactory. Not only was the molecular weight of the TPPS polymer too low for determination by membrane osmometry but also the yield was poor.

In the pure polysiloxanes both the dimethyl and the methylphenyl substituted polymers may be readily prepared and have been the subjects of much research work. Contrary to this, attempts to prepare polydiphenylsiloxane have met with many problems and no detailed preparation of pure high molecular weight polymer could be found. This pattern is again evident throughout the silphenylene-siloxane polymers. Polymers containing dimethyl or methylphenyl substituted silicon can be prepared with little difficulty by more than one method. When both substituents on the silicon are phenyl groups the polymerization encounters little success.

CHAPTER 4

THE THERMAL DEGRADATION OF RANDOM POLY(TETRAMETHYL-p-SILPHENYLENE - SILOXANE/DIMETHYLSILOXANE) COPOLYMERS AND OF THE POLY(TETRAMETHYL-p -SILPHENYLENE-SILOXANE) HOMOPOLYMER

4.1. Introduction

The replacement of varying amounts of oxygen atoms with p-phenylene groups in poly(dimethylsiloxane), DMS, is just one of the many modifications considered in the quest for improved siloxane-related polymers. Magill and his co-workers have studied several aspects of the behaviour of poly(tetramethyl-p-silphenylene-siloxane), TMPS, and block copolymers containing the TMPS and DMS monomer units. The thermal properties (Ref 40), the crystallization kinetics and morphology (Ref 41,42) and the chemical degradation by hydrofluoric acid (Ref 43,44) have been reported. However, not only is the information available on the thermal degradation limited but there is also some disagreement as to whether scission of the silphenylene (Ref 26) or the siloxane bond (Ref 24) is the primary mode of degradation.

The work described in this chapter compares the thermal stabilities of a series of random TMPS/DMS copolymers with those of the respective homopolymers, TMPS and DMS. The effect of the p-phenylene content is of interest. A variety of analytical techniques are used to study the action of heat on these polymers and the data recorded. On the basis

of the experimental results and a knowledge of previous work on related polymers a mechanism of thermal degradation is proposed.

4.2. Thermal analysis

1. TG

TG curves of the copolymer series are illustrated in Figure 4.1 together with those of TMPS and DMS. A single step weight loss occurs throughout the series. The general tendency was towards an increasing amount of residue as the p-phenylene content increased. No obvious trend was observed in the threshold degradation temperatures although it was appreciably higher than that of DMS in most cases.

2. DSC

Changes in the physical properties which result from a polymer passing through its glass transition temperature or melting temperature often occur before degradation. These transitions may be detected by a technique such as DSC which monitors enthalpy as a function of a programmed temperature change. This is useful in the comparison of a series of related polymers (Ref 45).

In the DSC trace (Fig 4.2) of TMPS an absorption of heat was observed at 140°. The absence of weight loss, changes in molecular weight or major structural changes led to the assumption that this endotherm represents the melting temperature of the polymer. Values ranging from 125° (Ref 18) to 159° (Ref 24) quoted in the literature for the melting temperature substantiate this claim. Although no further exothermic or endothermic spikes were observed, the

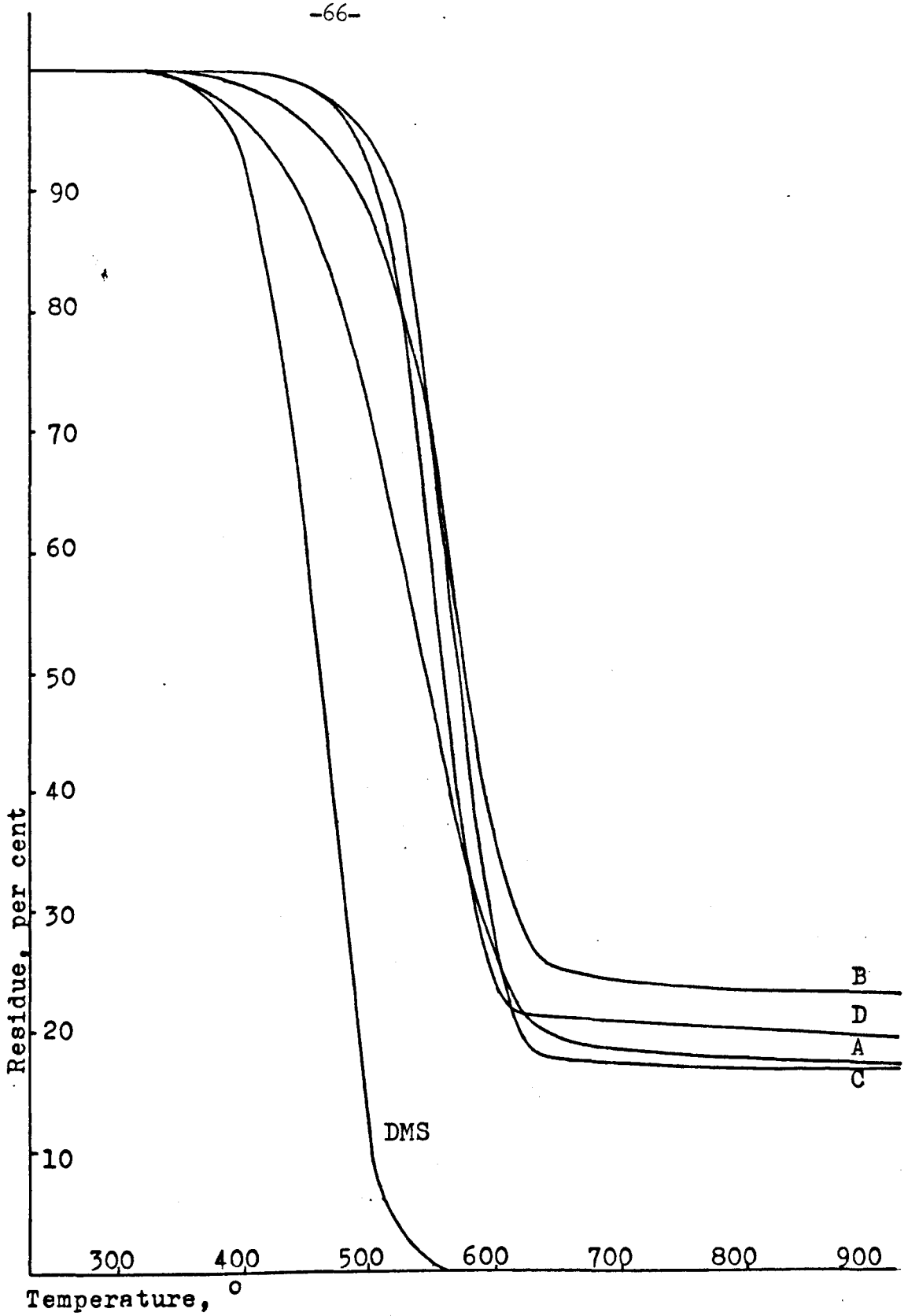


Fig. 4.1(a) TG traces for copolymers A, B, C and D and DMS.

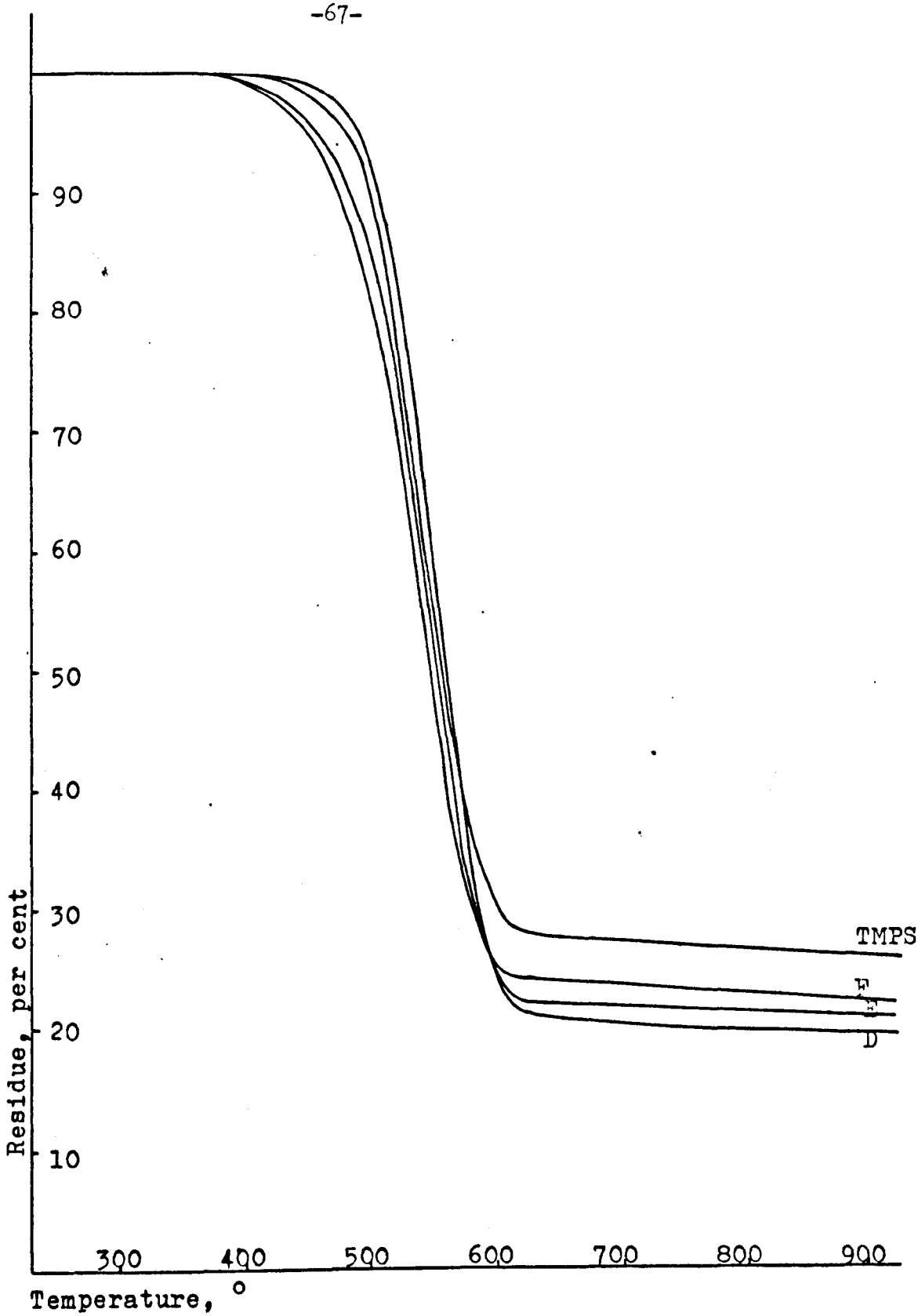


Fig. 4.1(b) TG traces for TMPS and copolymers D, E and F.

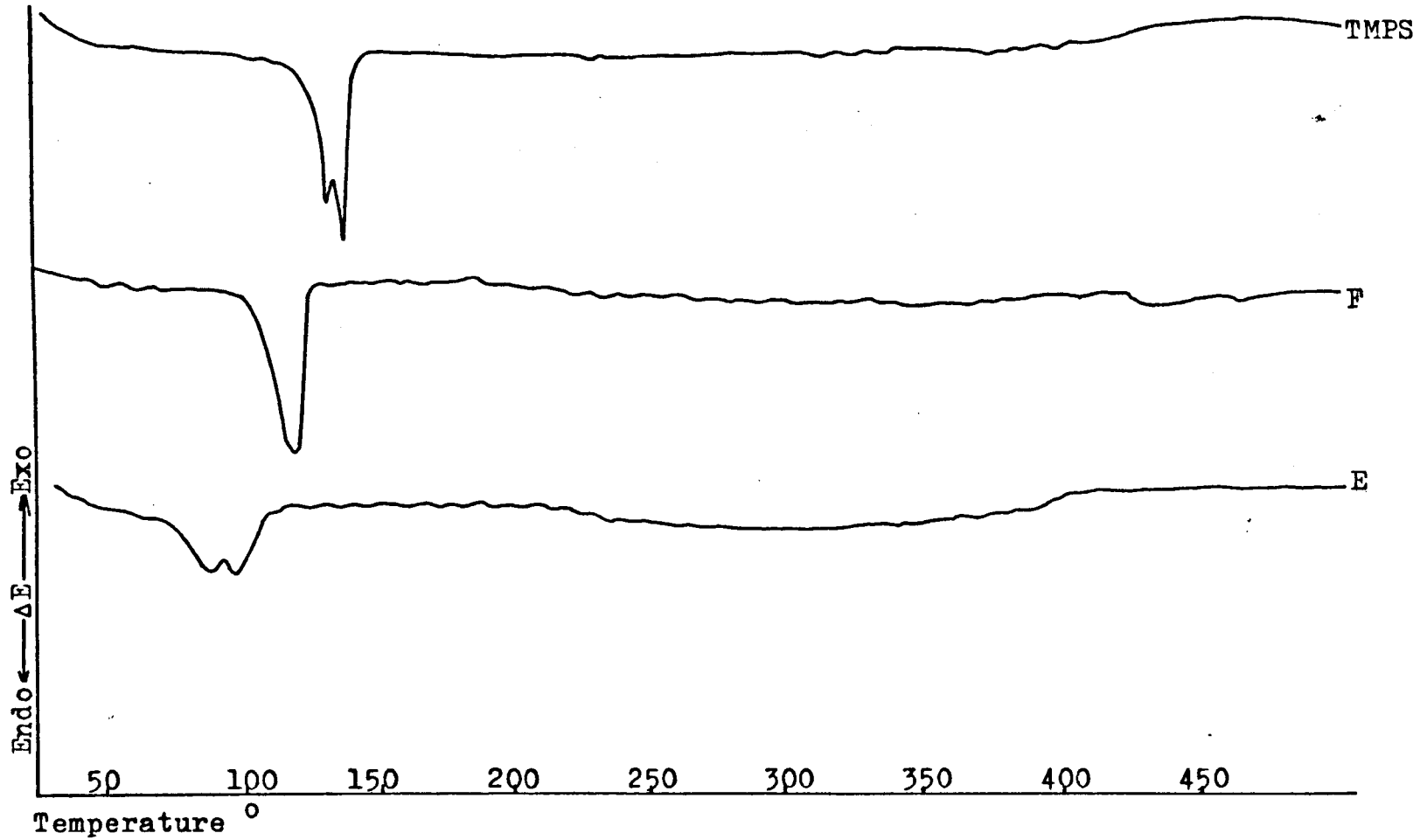


Fig. 4.2(a) DSC traces of TMPS and copolymers E and F.

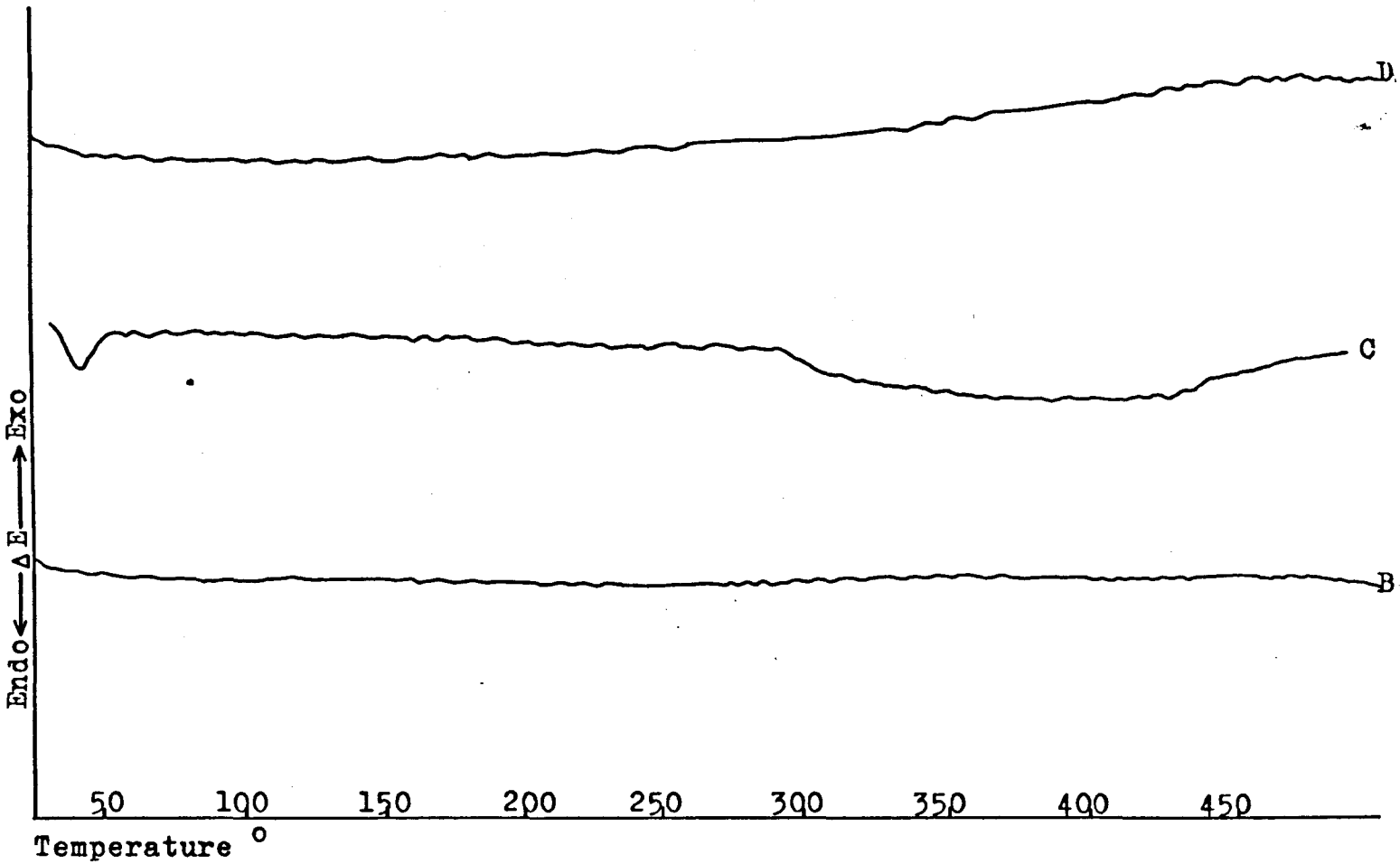


Fig. 4.2(b) DSC traces of copolymers B, C and D.

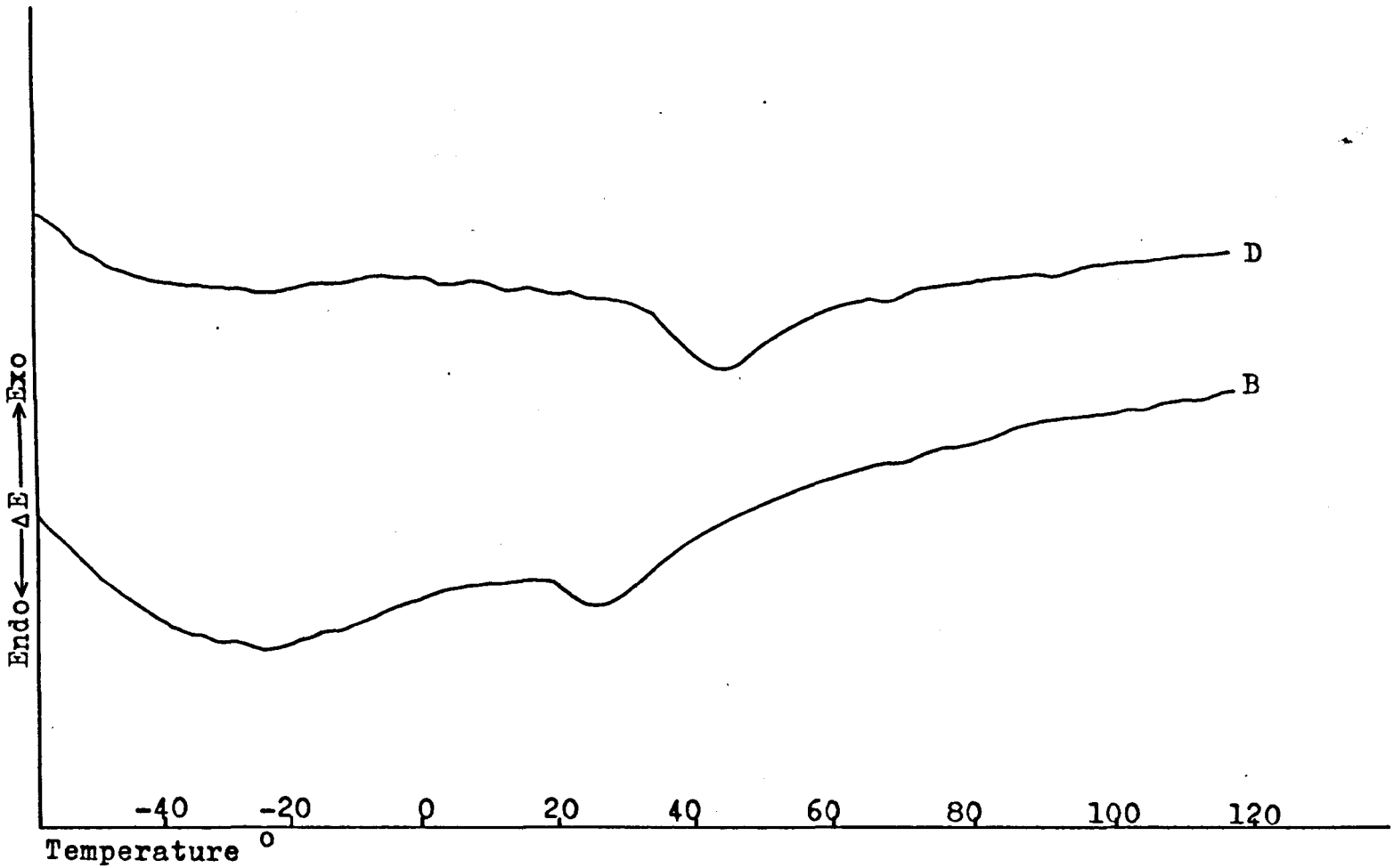


Fig. 4.2(c) DSC traces of copolymers B and D. Heating rate of 10^{o} min^{-1}.

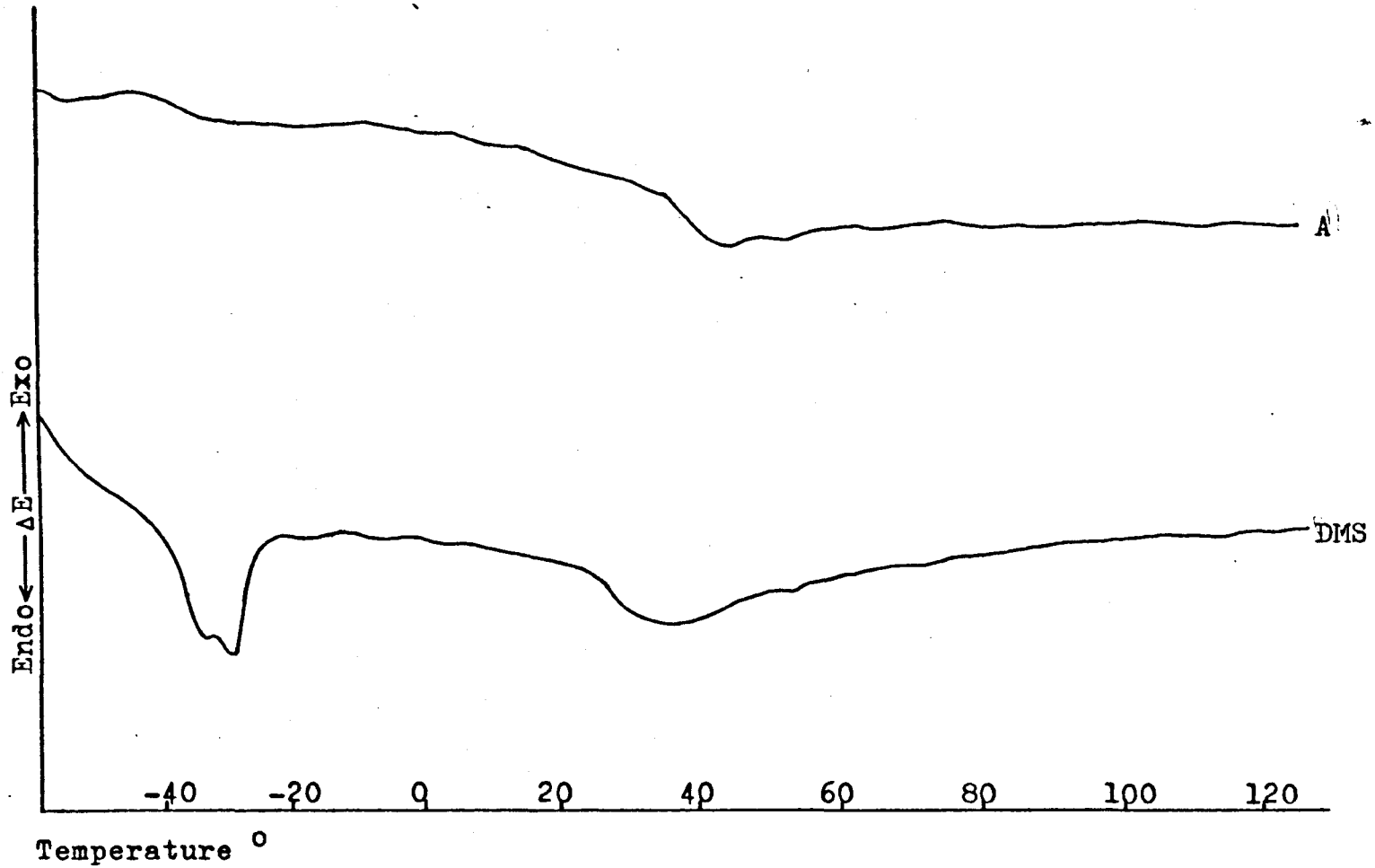


Fig. 4.2(d) DSC traces of copolymer A and DMS. Heating rate of $10^{o}min^{-1}$.

undulating nature of the remainder of the trace suggests that several low energy reactions occur throughout the degradation process.

Similar behaviour observed in the DSC traces of polymers A-F (Fig. 4.2) may be accounted for in the same manner. The position of the endotherm which represents the melting temperature decreases with increasing siloxane content. This trend is not unexpected in view of the dependence of the melting temperature on the siloxane content for TMPS/DMS block copolymers (Ref. 30).

3. TVA

The results of TVA experiments are shown in Figure 4.3. To facilitate comparison, the TVA trace from degrading DMS is presented in the same diagram. For DMS, evolution of volatiles commences at 343° and reaches a maximum at 443°. The replacement of a small number of oxygen atoms by p-phenylene groups as in polymers A and B raised both the threshold degradation temperature and the temperature at which evolution of volatiles reaches a maximum. The quantity of gaseous products was reduced. As the copolymer composition approaches that of TMPS, the TVA traces only move slightly from the base line at temperatures above 400°.

The "cold ring" fraction and the residue constituted the main fraction of the degradation products.

4.3. Analysis of Products from Isothermal Degradation.

Samples of the copolymers and TMPS were heated at temperatures up to 500° for different time intervals. The

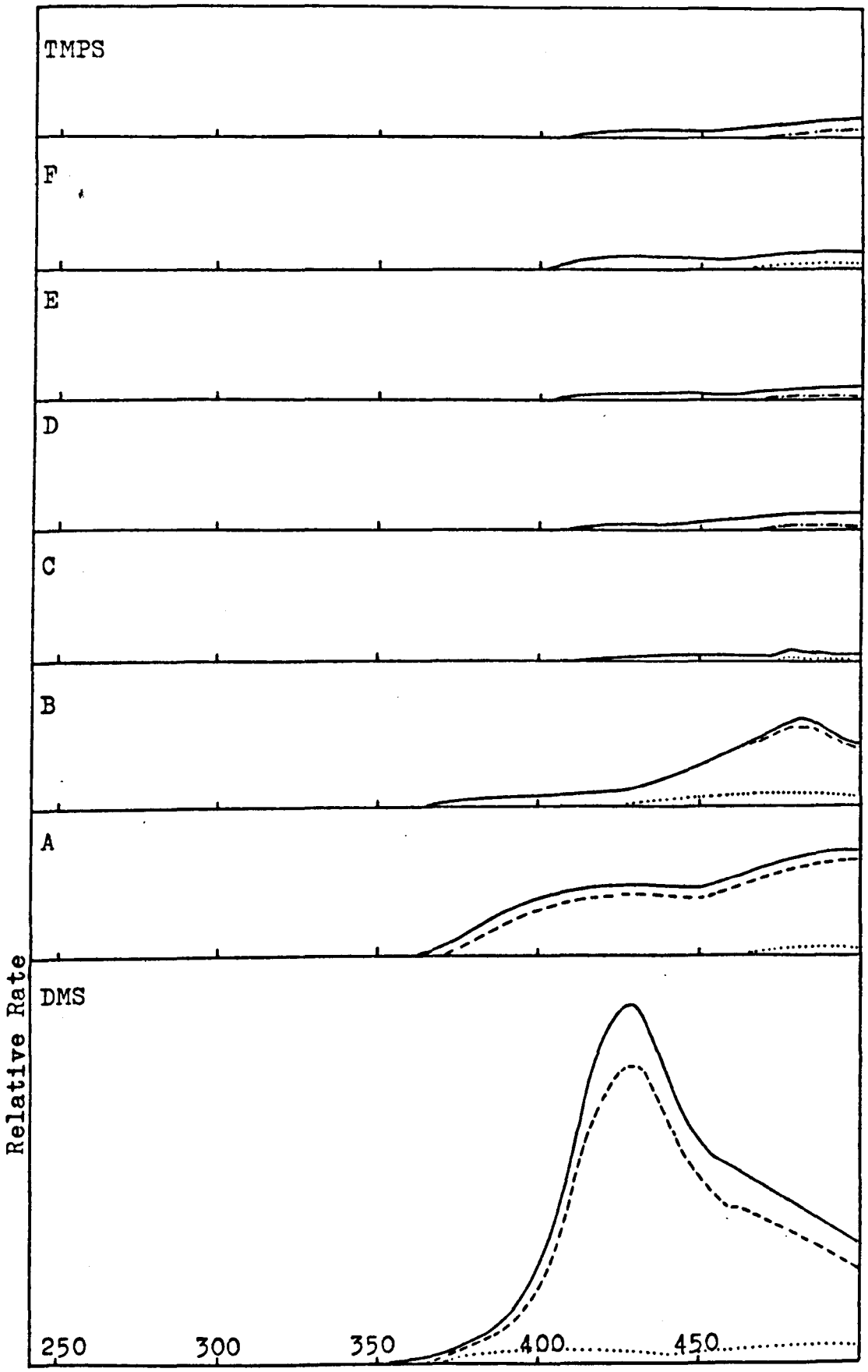


Fig. 4.3 TVA traces for the silphenylene-siloxane polymers and DMS.

Trap temperatures: 0°,—; -45°,---; -75°,····; -100°, -·-·-·-.

products of degradation were collected according to their volatilities and analyses were carried out.

1. Non-condensable products.

The thermograms from TVA experiments (Figure 4.3) suggest that no compounds volatile at -196° were formed. To verify this degradations were carried out in a closed system. No evidence of non-condensable material was detected after prolonged heating at 500°.

2. Condensable products

Infrared analysis

The infrared spectra of the gaseous products collected from degrading TMPS at 400°, 450° and 500° are illustrated in Figure 4.4. Corresponding spectra from copolymers A-F contained all the same bands and so only those from polymer F are illustrated as being typical (Figure 4.5). Spectra of the cyclic dimethylsiloxane trimer and tetramer are given in Figure 4.6.

Heating for prolonged periods up to 400° results in hexamethylcyclotrisiloxane (D_3) and octamethylcylotetrasiloxane (D_4) formation. At 450° new bands appear in the spectra which increase in intensity with increasing temperature. These new absorptions occur at 2130, 910, 885, 830 and 770 cm^{-1} and may be attributed to the Si-H group (2130, 910 and 885 cm^{-1}) and the $SiMe_3$ group (830 and 770 cm^{-1}). This would suggest that trimethylsilane is a product at 450° and above.

Ultraviolet analysis.

UV spectral measurements indicated that benzene was not

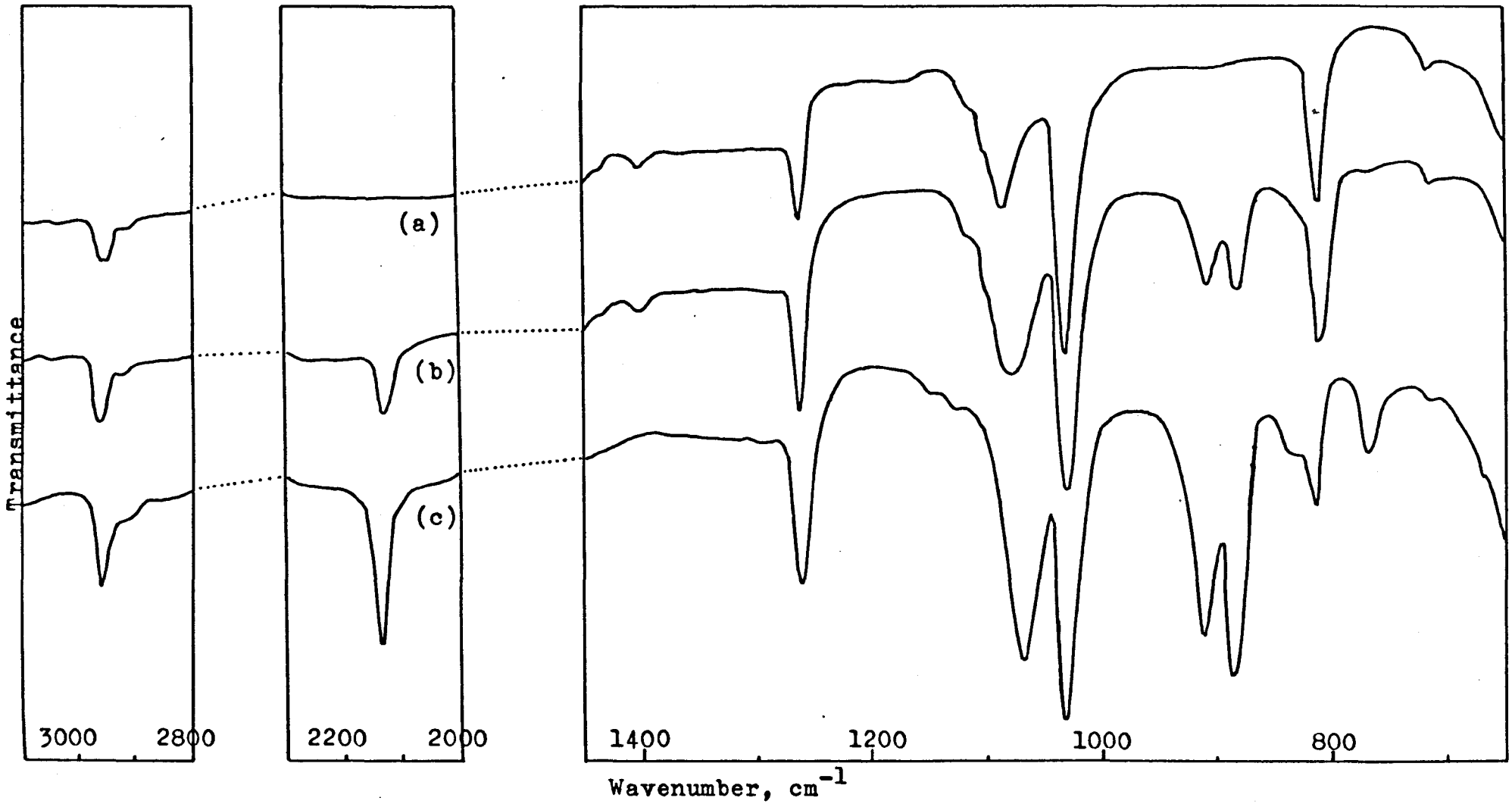


Fig. 4.4 Infrared spectra of the gaseous products from TMPS heated isothermally at: (a) 400°; (b) 450°; (c) 500°.

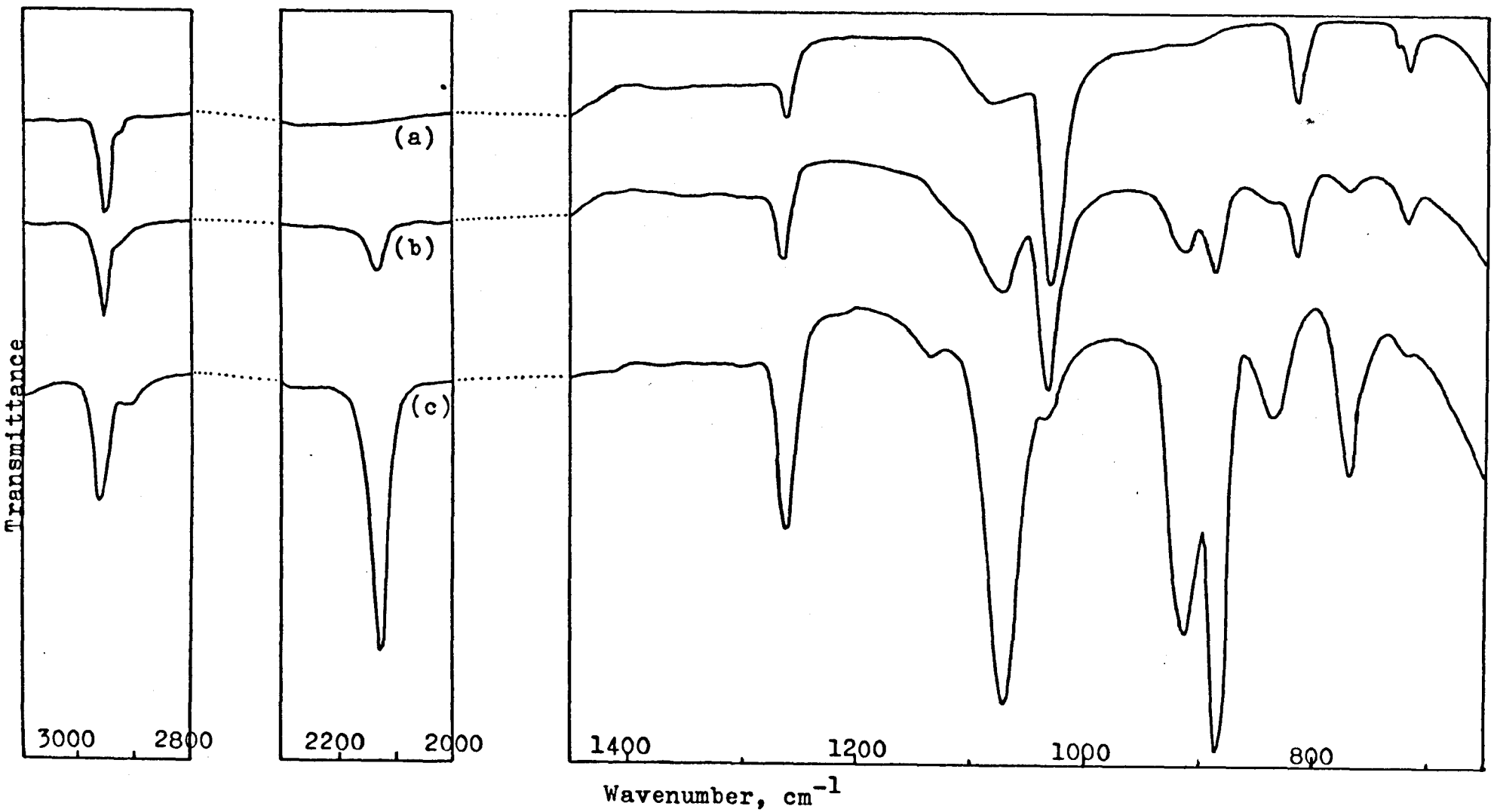


Fig. 4.5 Infrared spectra of the gaseous products from polymer F heated isothermally at: (a) 400°; (b) 450°; (c) 500°.

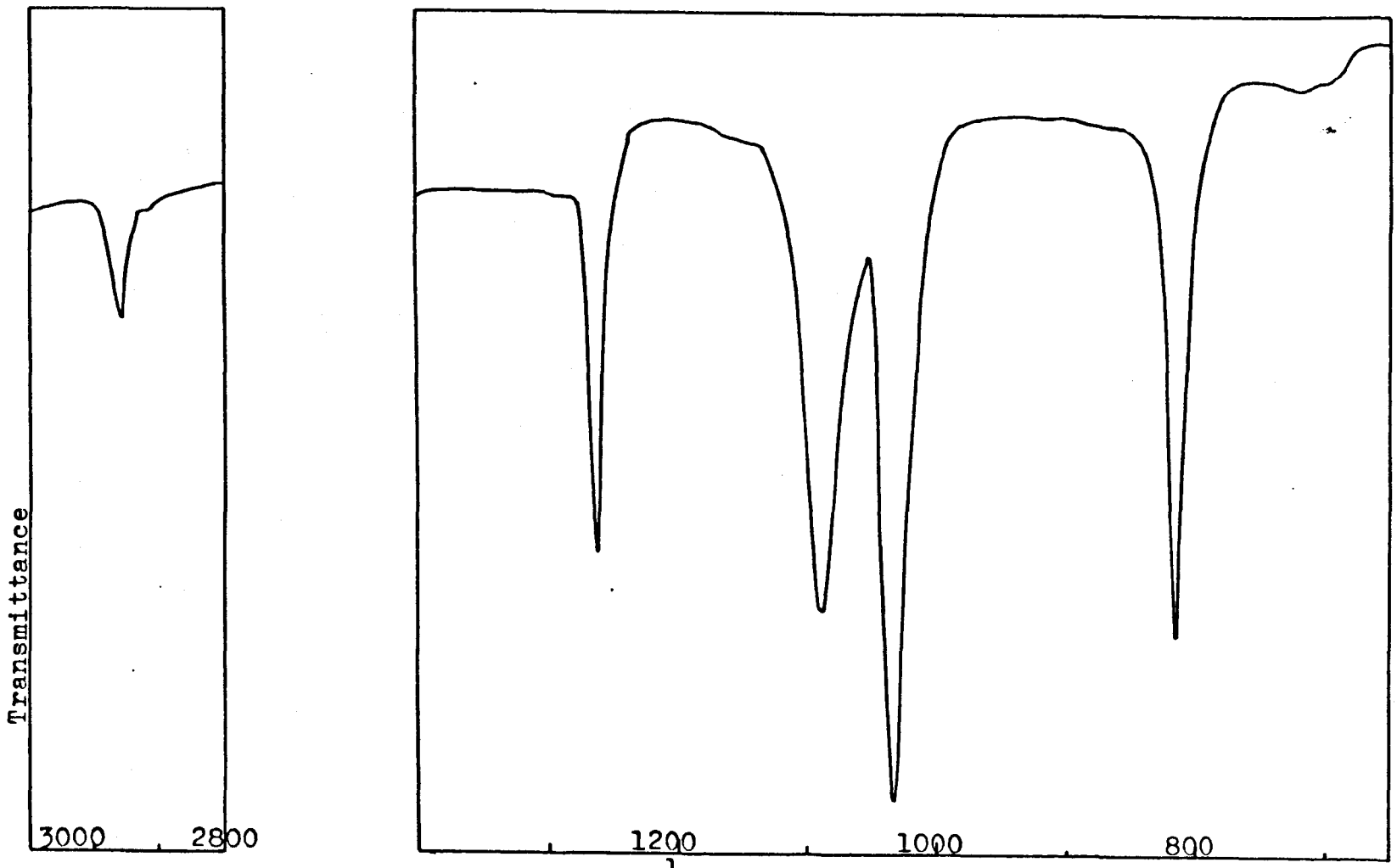


Fig. 4.6 Infrared spectrum of cyclic dimethylsiloxane trimer and tetramer.

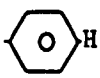
produced in the reaction.

GCMS

A typical gas chromatogram of the gaseous products is given in Figure 4.7. Mass spectra of peaks 1, 2 and 3 were recorded (Figure 4.8). The products were identified as the cyclic dimethylsiloxane trimer and tetramer and trimethylsilane which is in accord with the infrared analysis.

3. "Cold ring" fraction

Infrared analysis

The effect of temperature on the infrared spectrum of the TMPS "cold ring" fraction is illustrated in Figure 4.9. At 400° the spectrum is almost indistinguishable from that of the starting material. At 450° and above the formation of the Si-H group was indicated by the appearance of two new absorption bands at 2150 and 910 cm^{-1}. A third new band at 1600 cm^{-1} suggested that the  H group was also produced.

Since these observations apply to each of the TMPS/DMS copolymers it was not considered necessary to illustrate the spectra from every sample. The infrared spectra for polymer C is given in Figure 4.10 and is typical.

GC

Gas chromatograms of the "cold ring" fractions from polymers A-F and TMPS degraded at 500° for 1 hour are compared in Figures 4.11 and 4.12. Initially there appeared to be little or no connection between them and the number of products to be identified was large. However by considering the effect of both the p-phenylene content and the temperature of degradation on the products formed, the interpretation was

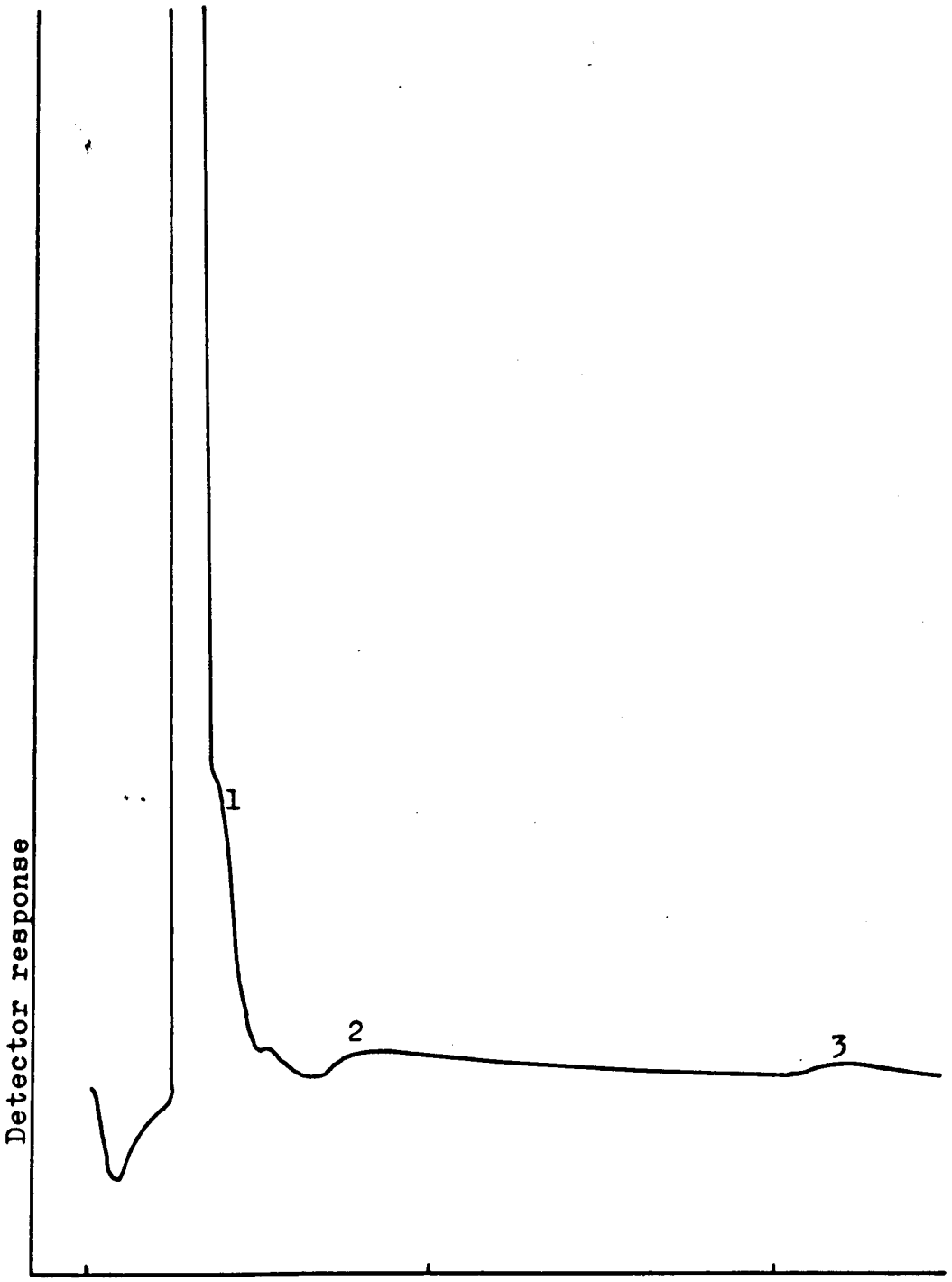


Fig. 4.7 Gas chromatogram (from GCMS) of the gaseous products of degradation of the silphenylene-siloxane polymers.

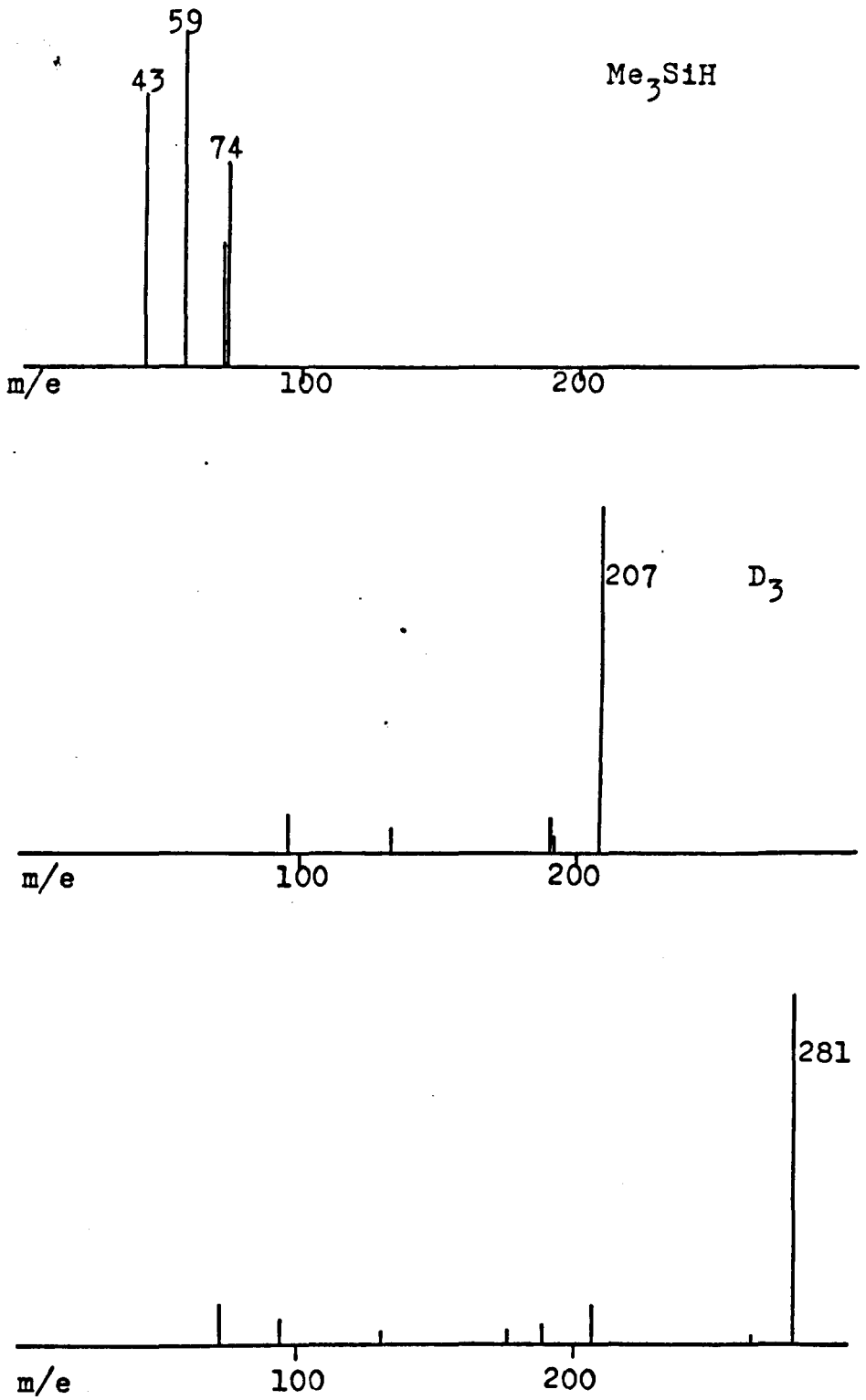


Fig. 4.8 Mass spectra (from GCMS) of the gaseous products of degradation of the silphenylene-siloxane polymers.

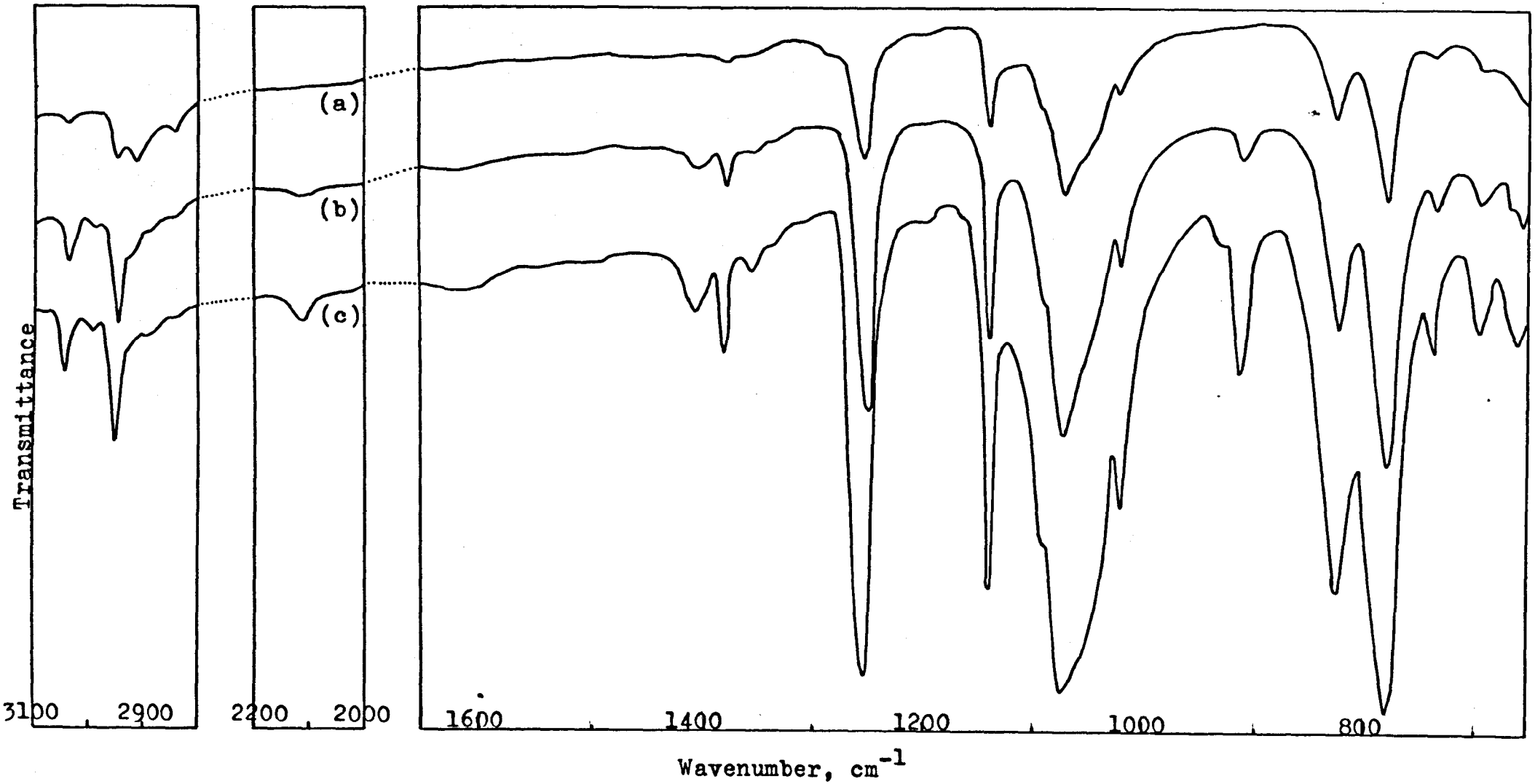


Fig. 4.9 Infrared spectra of 'cold ring' fractions from TMPS heated isothermally at: (a) 400°; (b) 450°; (c) 500°.

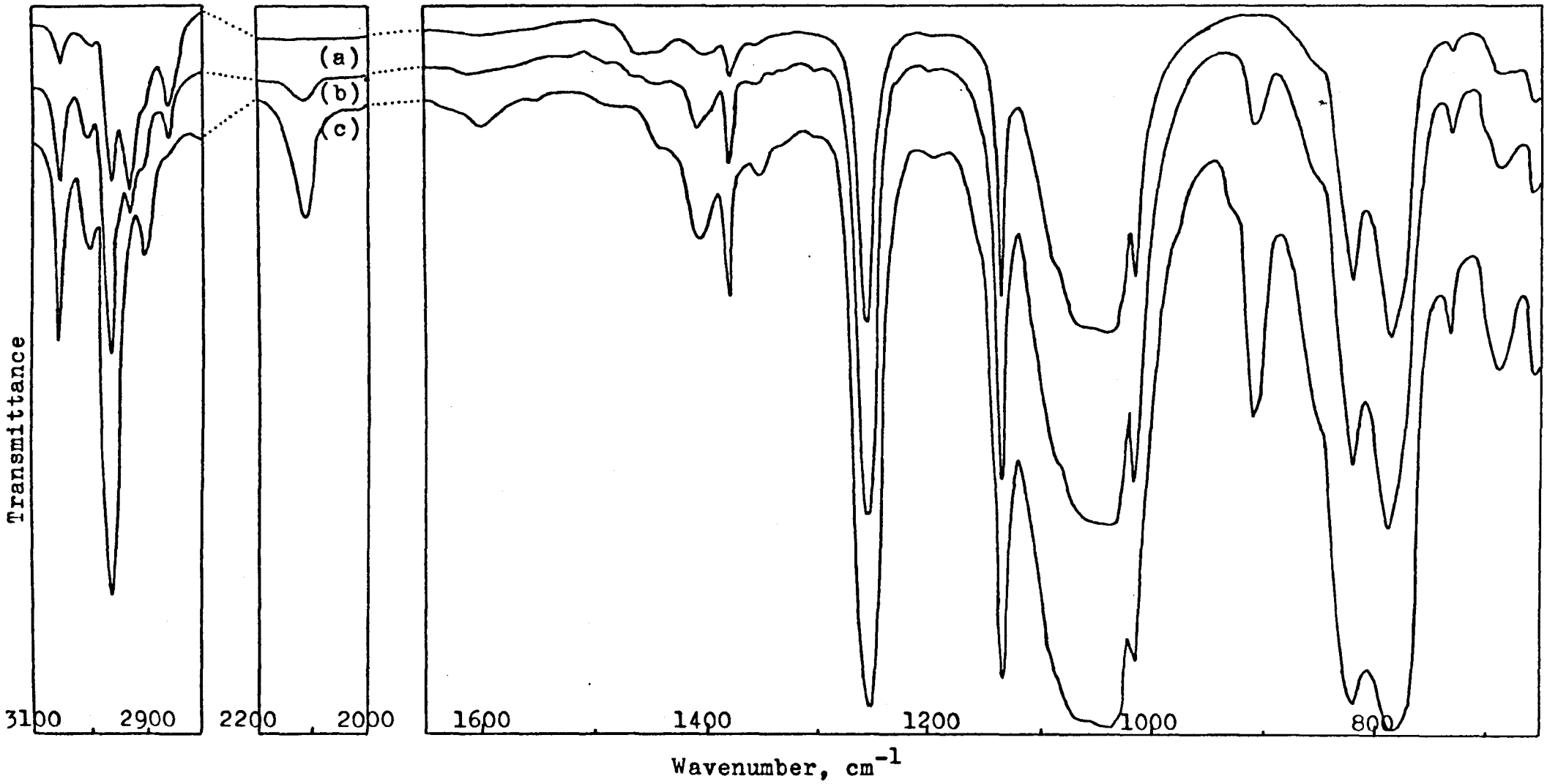


Fig. 4.10 Infrared spectra of 'cold ring' fractions from polymer C heated isothermally at: (a) 400°; (b) 450°; (c) 500°.

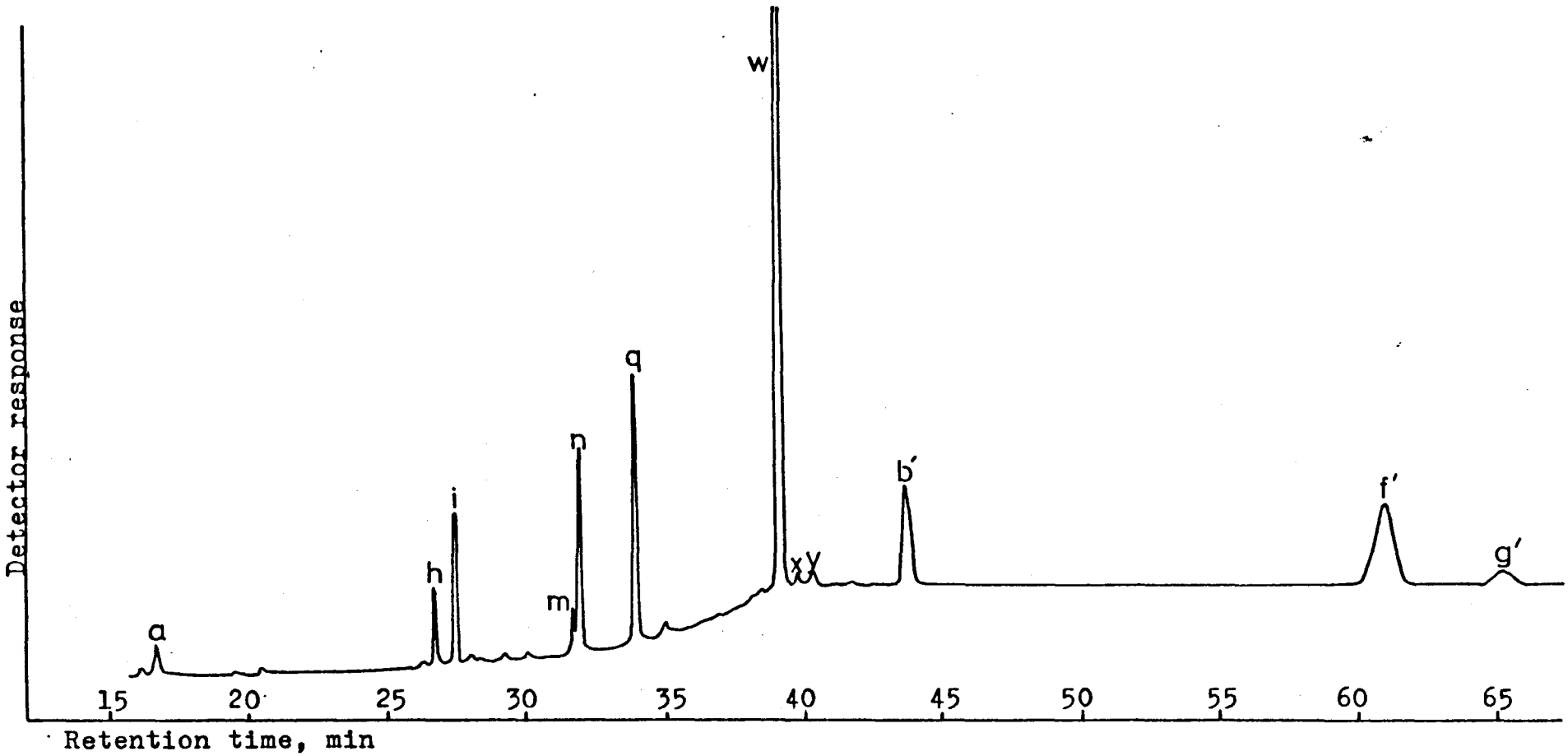


Fig. 4.11(a) GC trace of the products of degradation of TMPS (1h at 500°). Programme, 5° min^{-1} from 50° to 270°, thereafter held at 270°.

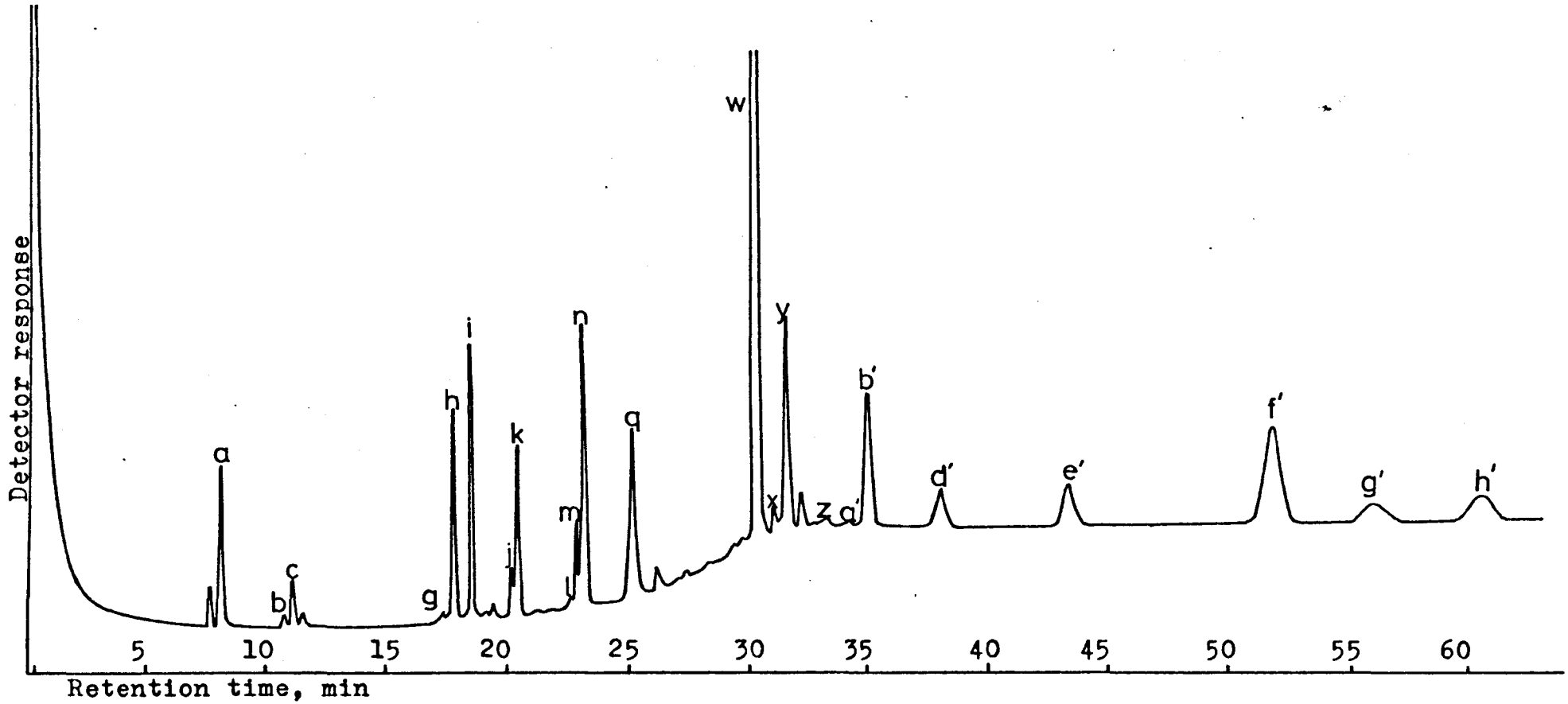


Fig. 4.11(b) GC trace of the products of degradation of polymer F (1h at 500°). Programme, 5° min^{-1} from 100° to 270°, thereafter held at 270°.

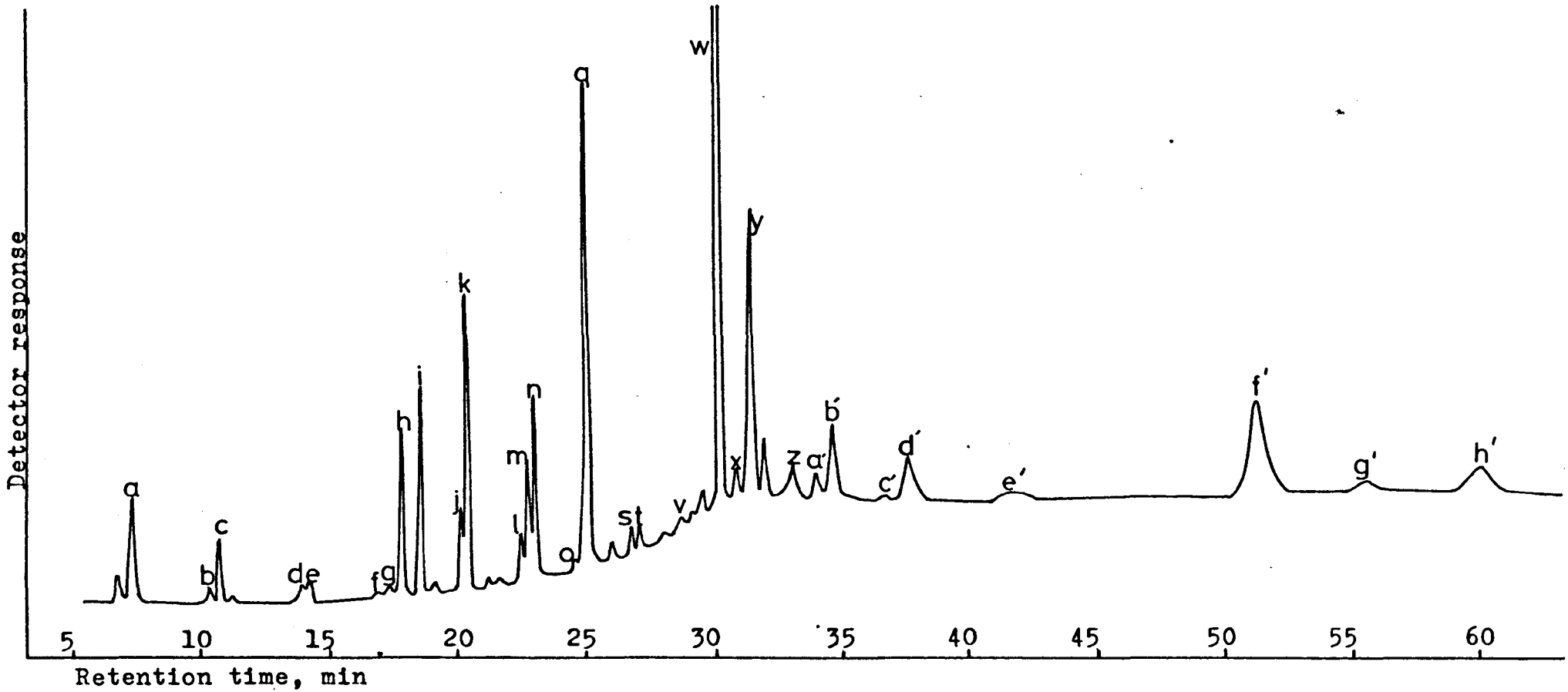


Fig. 4.11(c) GC trace of the products of degradation of polymer E (1h at 500°). Programme, 5° min^{-1} from 100°to 270°, thereafter held at 270°.

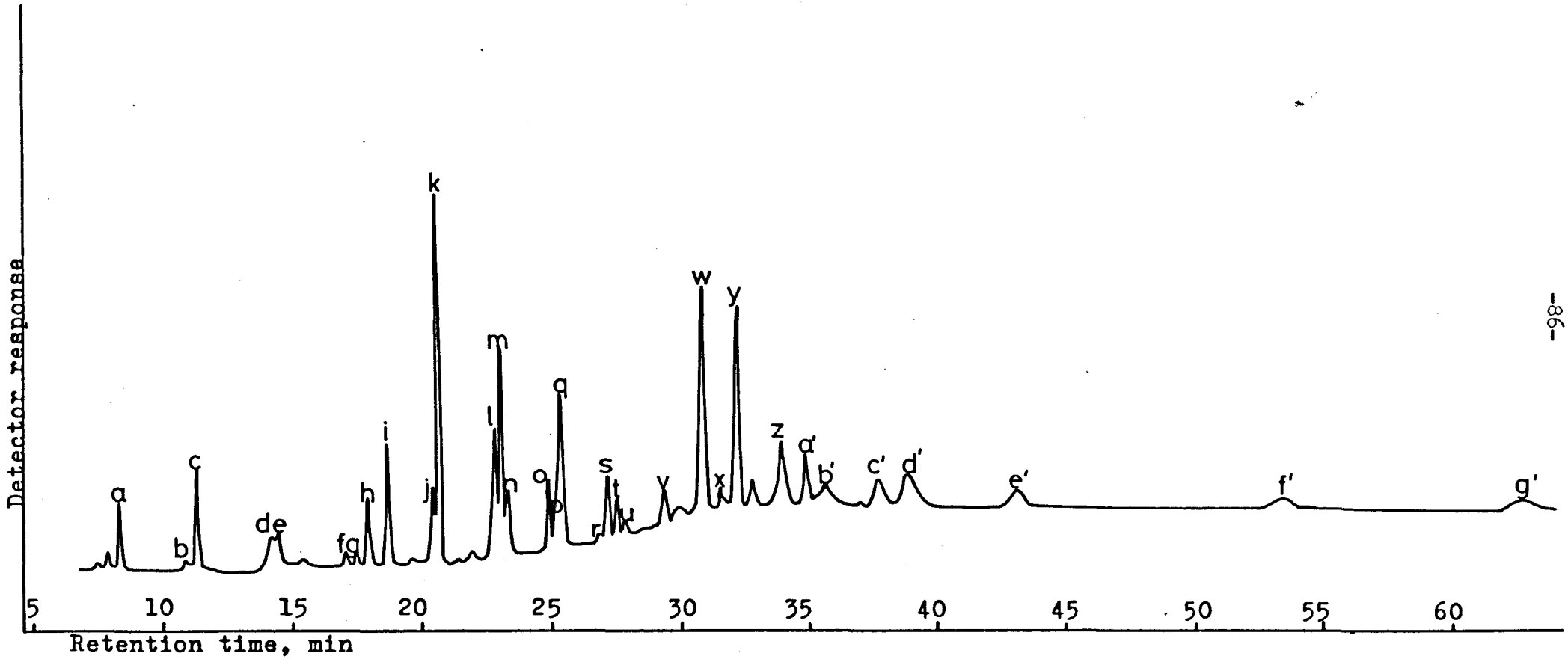


Fig. 4.11(d) GC trace of the products of degradation of polymer D (1h at 500°). Programme, 5° min^{-1} from 100° to 270°, thereafter held at 270°.

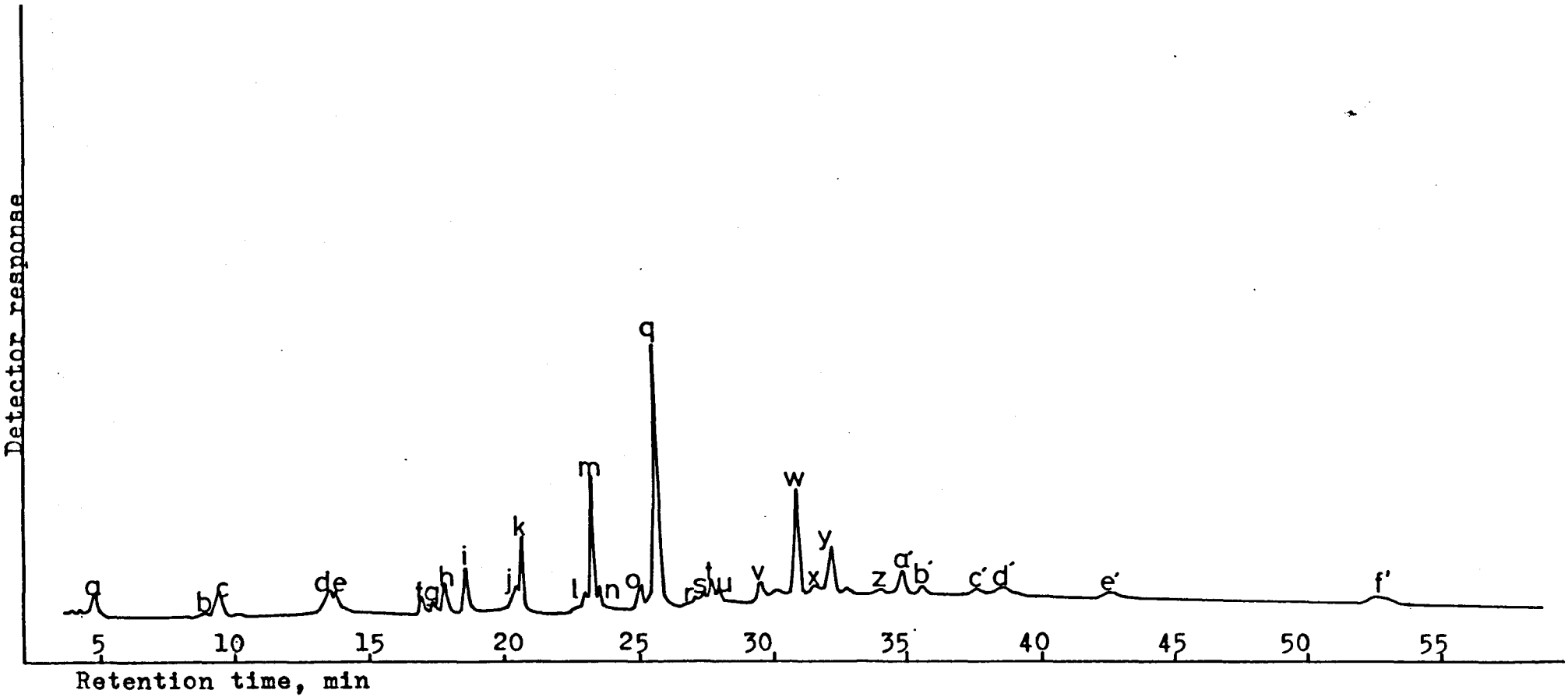


Fig. 4.11(e) GC trace of the products of degradation of polymer C (1h at 500°). Programme, 5° min^{-1} from 100° to 270°, thereafter held at 270°.

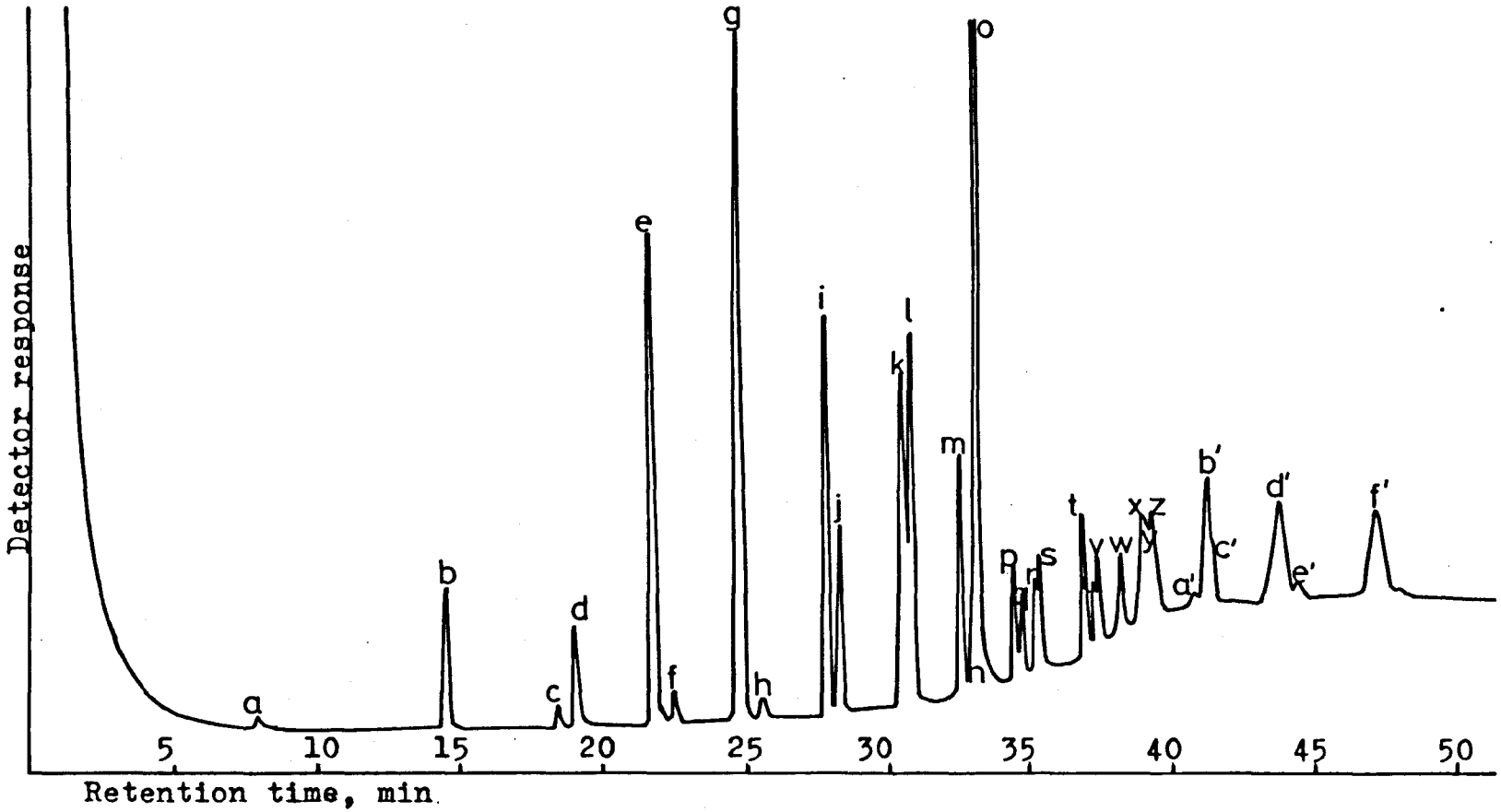


Fig. 4.12(a) GC trace of the products of degradation of polymer A (1h at 500°). Programme, 5° min^{-1} from 50° to 270°, thereafter held at 270°.

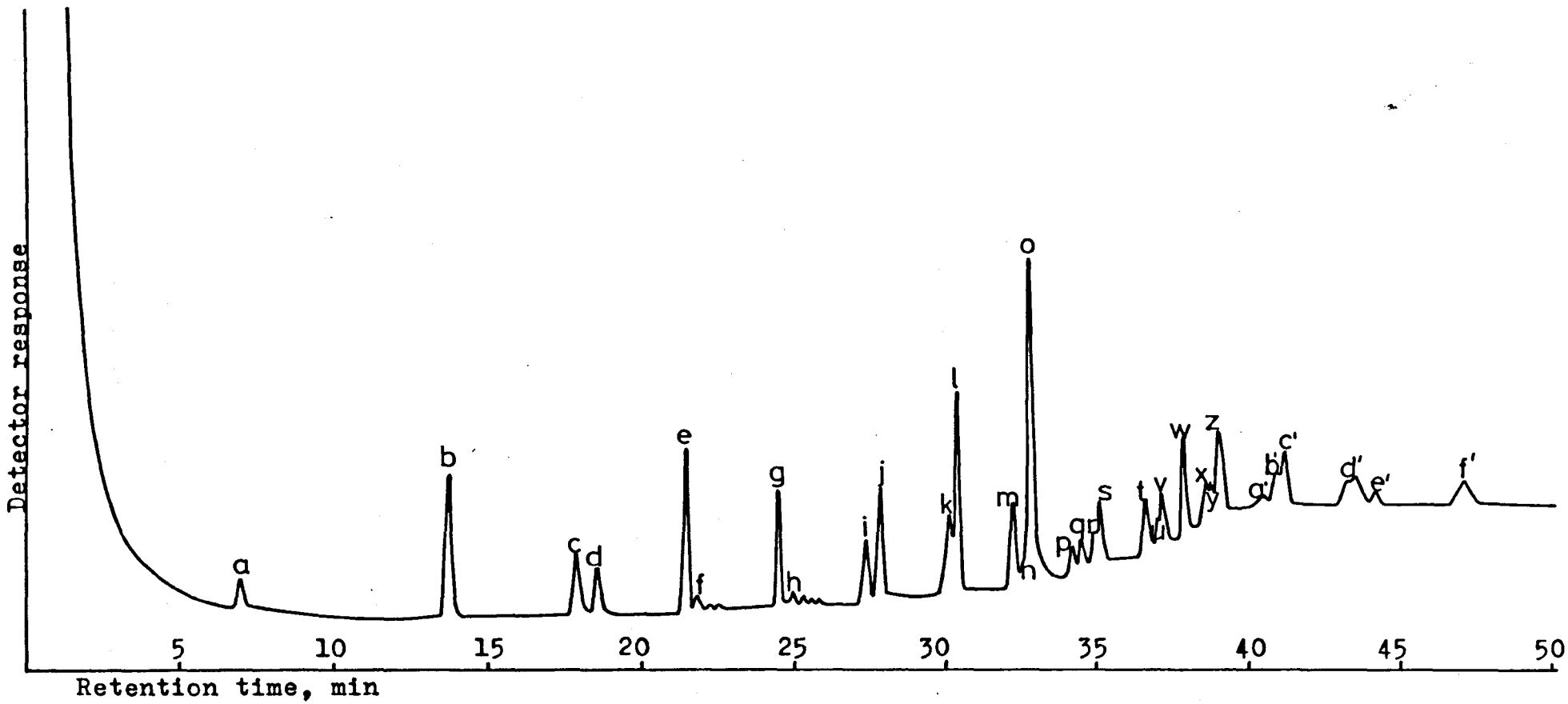


Fig. 4.12(b) GC trace of the products of degradation of polymer B (1h at 500°). Programme, 5° min^{-1} from 50° to 270°, thereafter held at 270°.

simplified.

Samples were dissolved in anhydrous diethyl ether prior to injecting into the GC column. After analysing the "cold ring" fraction from two of the polymers individually, they were combined and a chromatogram of the mixture was recorded. By comparing the initial GC traces with that of the mixture, the products common to both samples were determined. This process was repeated for several combinations and many of the products were found to originate from more than one polymer.

Each polymer was degraded at 350°, 400°, 450° and 500° and the "cold ring" fractions were collected and analysed. It was noted that in the case of polymers A and B, the majority of the products making up the "cold ring" fraction were prsent from 350° upwards whereas several of the compounds produced from polymers C-F appear at only 450° and above.

GCMS

After carrying out the GC analysis described above, more positive identification of the products was made using GCMS. Mass spectra of the different peaks were recorded and the m/e values for the parent ions with their proposed structures are listed in Tables 4.1 and 4.2.

Summary of products

The structures of the products were proposed after consideration of experimental results of various kinds, namely:

(a) the m/e values of the parent ions for the peaks present in the GCMS analysis,

(b) the effect of temperature on the products formed,

TABLE 4.1

GCMS analysis of a mixture of degradation products from TMPS and TMPS/DMS copolymers C, D, E and F.

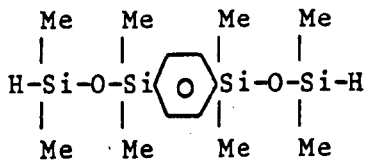
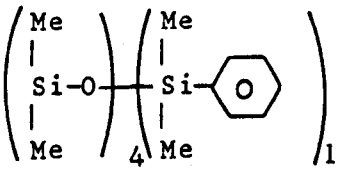
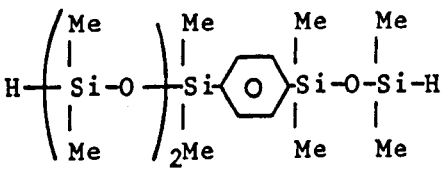
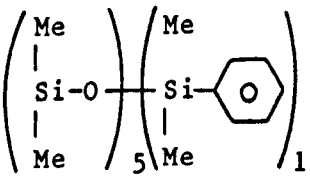
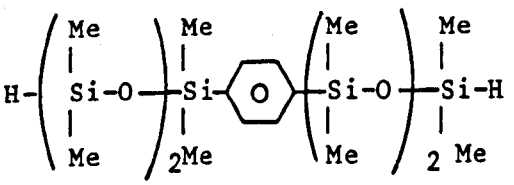
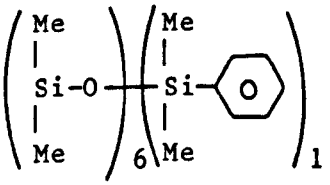
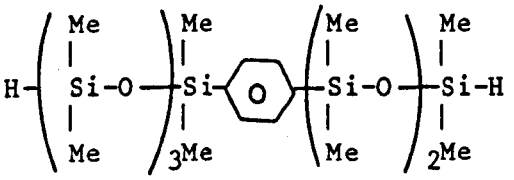
Peak	m/e of parent ion	Proposed structure
a	342	
b	430	
c	416	
d	489(M-15)	
e	Not recorded*	
f	563(M-15)	
g	Not recorded*	

TABLE 4.1 (contd.)

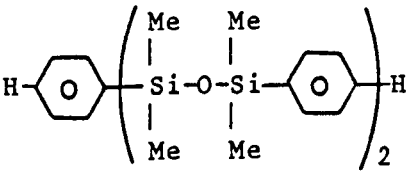
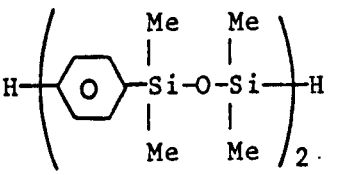
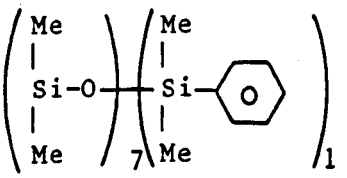
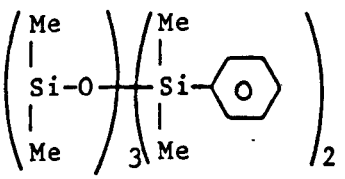
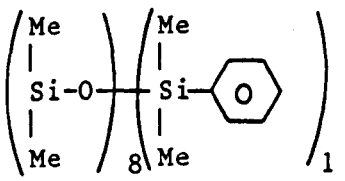
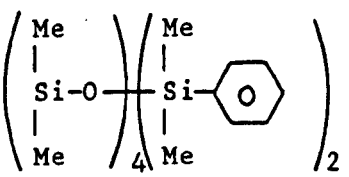
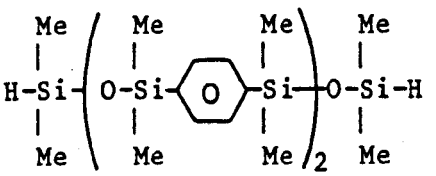
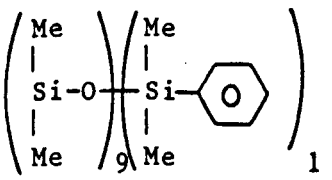
Peak	m/e of parent ion	Proposed structure
h	417(M-77)	
i	417(M-1)	
j	637(M-15)	
k	475(M-15)	
l	711(M-15)	
m	564	
n	550	
o	697(M-103	

TABLE 4.1 (contd.)

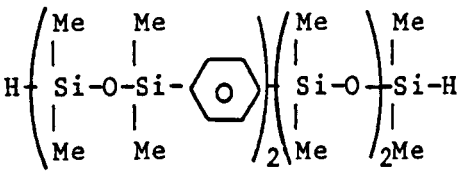
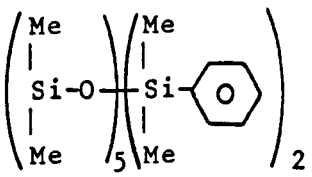
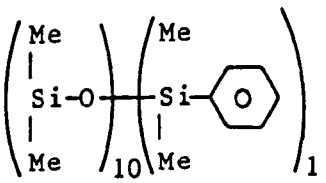
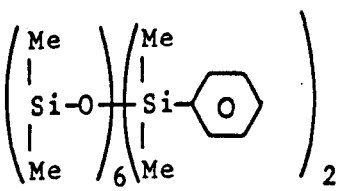
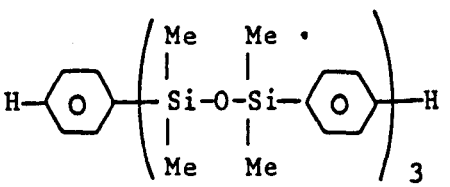
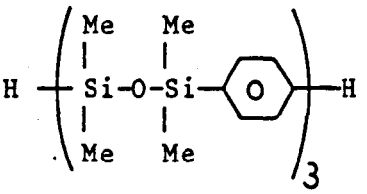
Peak	m/e parent ion	Proposed structure
p	624	
q	623(M-15)	
r	Not recorded*	
s	Not recorded	?
t	Not recorded	?
u	712	
v	Not recorded	?
w	625(M-77)	
x	625(M-1)	

TABLE 4.1 (contd.)

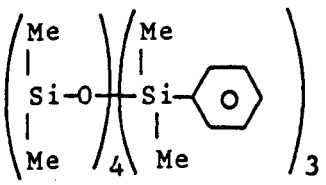
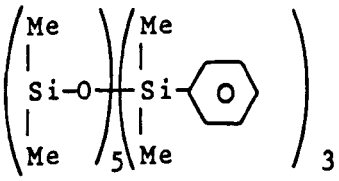
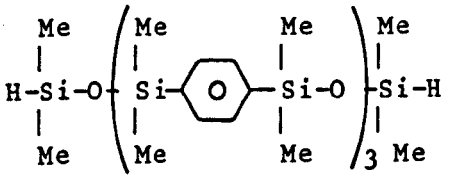
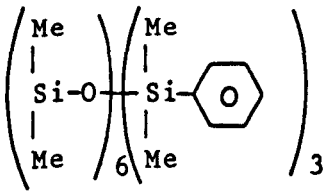
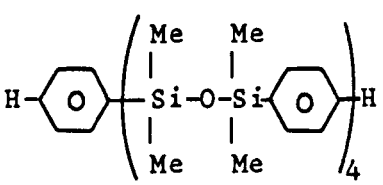
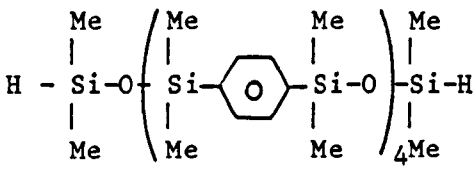
Peak	m/e of parent ion	Proposed structure
y	698	
z	Not recorded*	
a'	Not recorded	?
b'	758	
c'	Not recorded*	
d'	Not recorded	?
e'	Not recorded	?
f'	833(M-77)	

TABLE 4.1 (contd.)

Peak	m/e of parent ion	Proposed structure
g'	741(M-225)	

* Proposed structure on basis of the retention time, Rt.

TABLE 4.2

GCMS analysis of a mixture of degradation products from TMPS/DMS copolymers A and B.

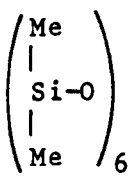
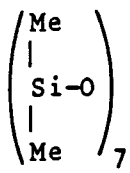
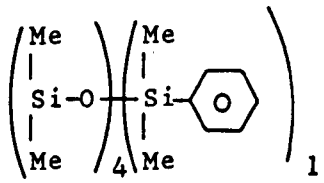
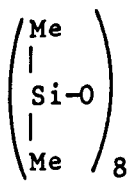
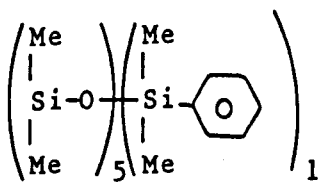
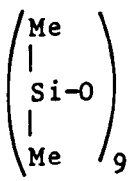
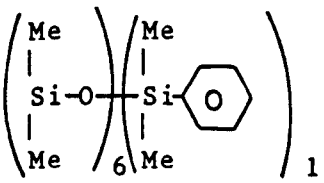
Peak	m/e of parent ion	Proposed structure
a	429(M-15)	
b	503(M-15)	
c	430	
d	577(M-15)	
e	489(M-15)	
f	429(M-15-D_3)	
g	563(M-15)	

Table 4.2 (contd.)

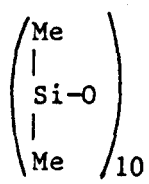
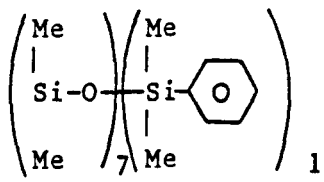
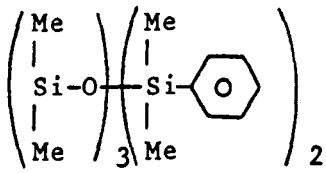
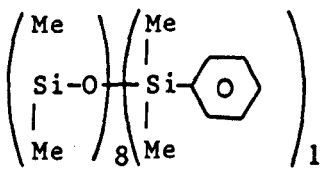
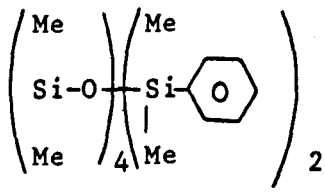
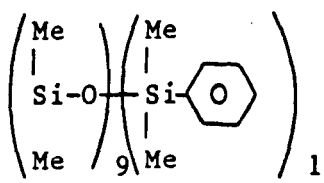
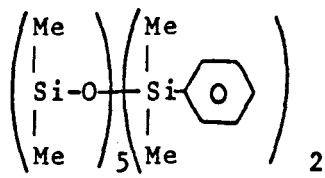
Peak	m/e of parent ion	Proposed structure
h	503(M-15-D_3)	
i	637(M-15)	
j	475(M-15)	
k	711(M-15)	
l	564	
m	697(M-103)	
n	Not recorded	Compound containing Si-H group.
o	623(M-15)	

TABLE 4.2 (contd.)

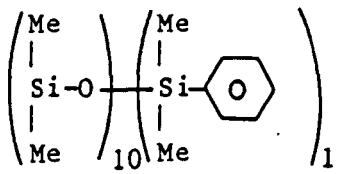
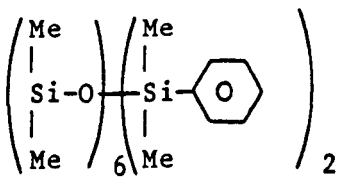
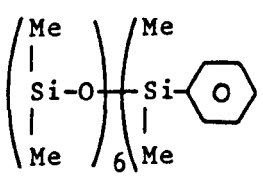
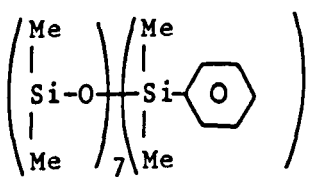
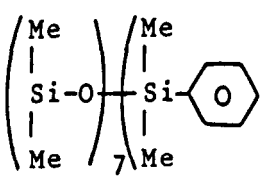
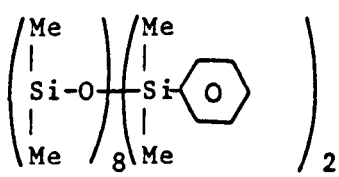
Peak	m/e of parent ion	Proposed structure
p	Not recorded*	
q	712	
r	Not recorded	?
s	Not recorded*	 Isomer of q
t	786	
u	Not recorded*	 Isomer of t
v	Not recorded	?
w	Not recorded	?
x	623(M-15-D_3)	

TABLE 4.2 (contd.)

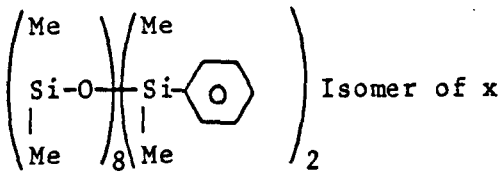
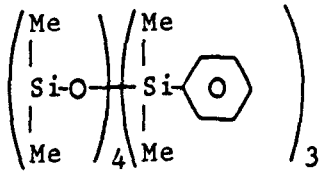
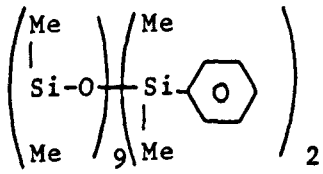
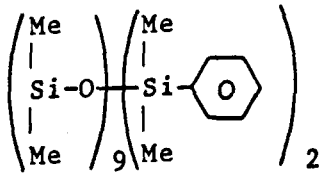
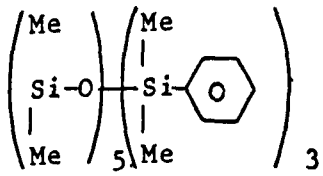
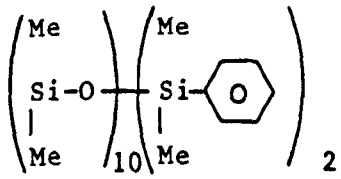
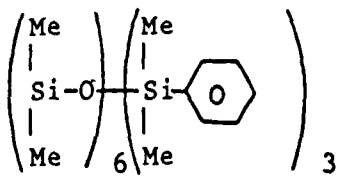
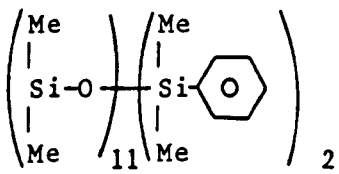
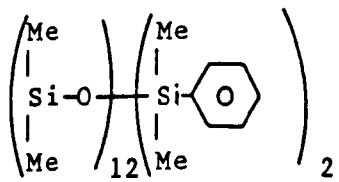
Peak	m/e of parent ion	Proposed structure
y	860	 Isomer of x
z	Not recorded*	
a'	503	
b'	Not recorded*	
c'	Not recorded*	
d'	771(M-15-D_3)	
e'	Not recorded*	

TABLE 4.2 (contd.)

Peak	m/e of parent ion	Proposed structure
f'	Not recorded*	
g'	Not recorded*	

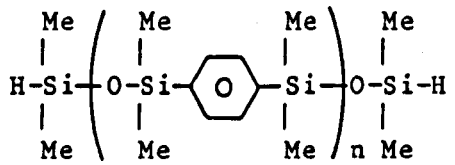
*Proposed structure on basis of the retention time, Rt.

(c) the effect of polymer composition on the products formed,

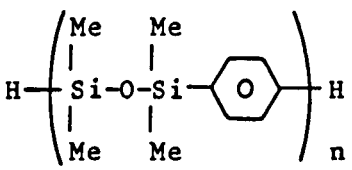
(d) the temperature dependence of the infrared spectra,

(e) when a homologous series was proposed, a plot of Rt against molecular weight was made.

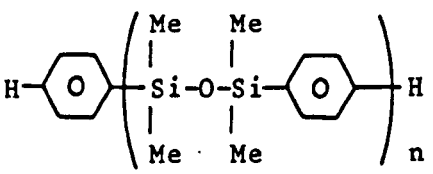
The proposed structures for the degradation products from TMPS are summarised as follows:



A



B



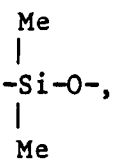
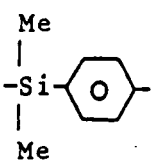
C

A and B were present only after degradation at 450° upwards. C was detected at 400° but increased considerably at the higher temperatures.

Increasing the siloxane content in the polymer results in an increasing siloxane content in the short chain oligomers. As the copolymer composition tends towards that of DMS, cyclic oligomers are formed in preference to the linear short chain fragments. This was noticed for polymers A and B where the following series of cyclic oligomers were observed from the

onset of volatolization,

D_n ; D_nP_1 ; D_nP_2 ; D_nP_3

D represents  , P represents 

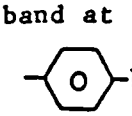
Graphs of retention time, Rt, versus molecular weight for series of oligomers are plotted in Figure 4.13.

4. Residue

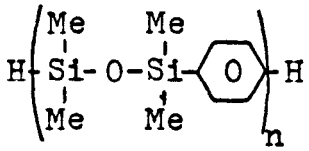
Infrared analysis

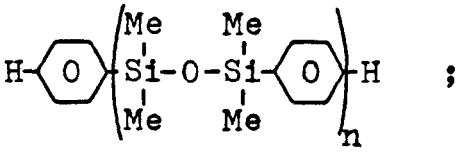
Residues from a silphenylene containing polymer degraded at temperatures below 350° are soluble so that the infrared spectra may be recorded using thin films cast on sodium chloride discs. Such spectra were almost indistinguishable from those of the starting materials as shown in Figures 4.14 and 4.15.

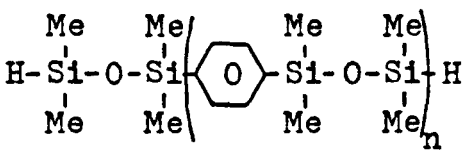
Degradation at temperatures between 350° and 400° results in the formation of an insoluble or gel fraction. In this case the KBr disc technique was employed. Again no obvious differences were detected between these spectra and those of the original polymer (Figures 4.14 and 4.15).

Spectral analysis of both the "cold ring" fraction and the gaseous products revealed that Si-H formation resulted when the degradation temperature was 450° or higher. This was again the case in the residue. In Figures 4.14 and 4.15 the characteristic bands of the Si-H group at 2150, 910 and 890 cm^{-1} appear at 450° and increase in intensity at 500°. As in the "cold ring" fraction the band at 1600 cm^{-1} becomes apparent. This band, distinctive of the  -H group, was most intense in the residue from polymers

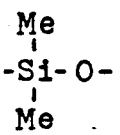
Key to Fig. 4.13.

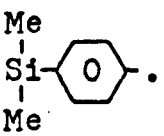
(a) •  ;

o  ;

+  .

(b) + D_n; o D_nP_1; × D_nP_2; • D_nP_3;

where D represents 

and P represents  .

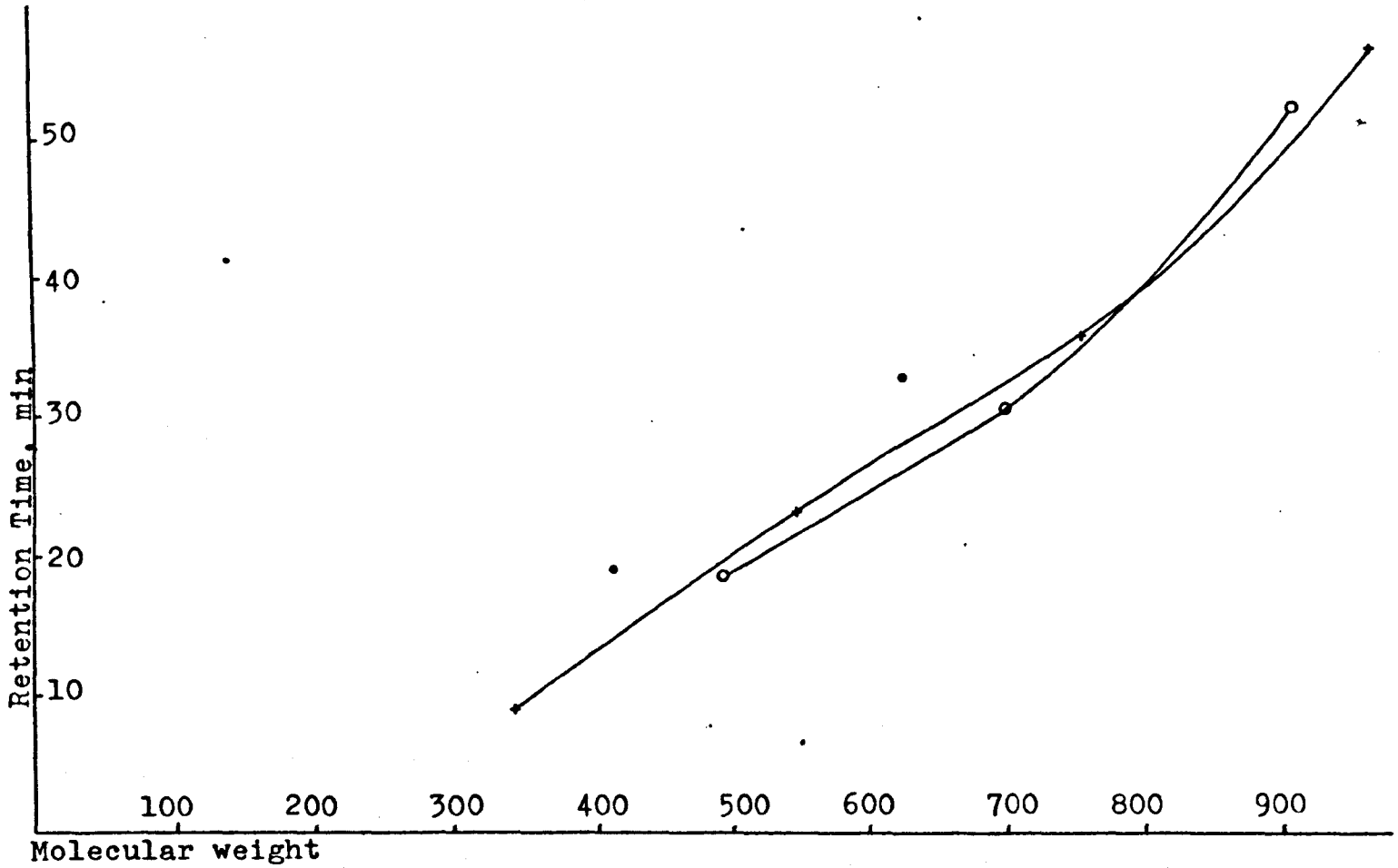


Fig. 4.13(a) Retention time versus molecular weight of the non-cyclic degradation products of TMPS heated to 500°. Programme, 5° min^{-1} from 50° to 270°, thereafter held at 270°.

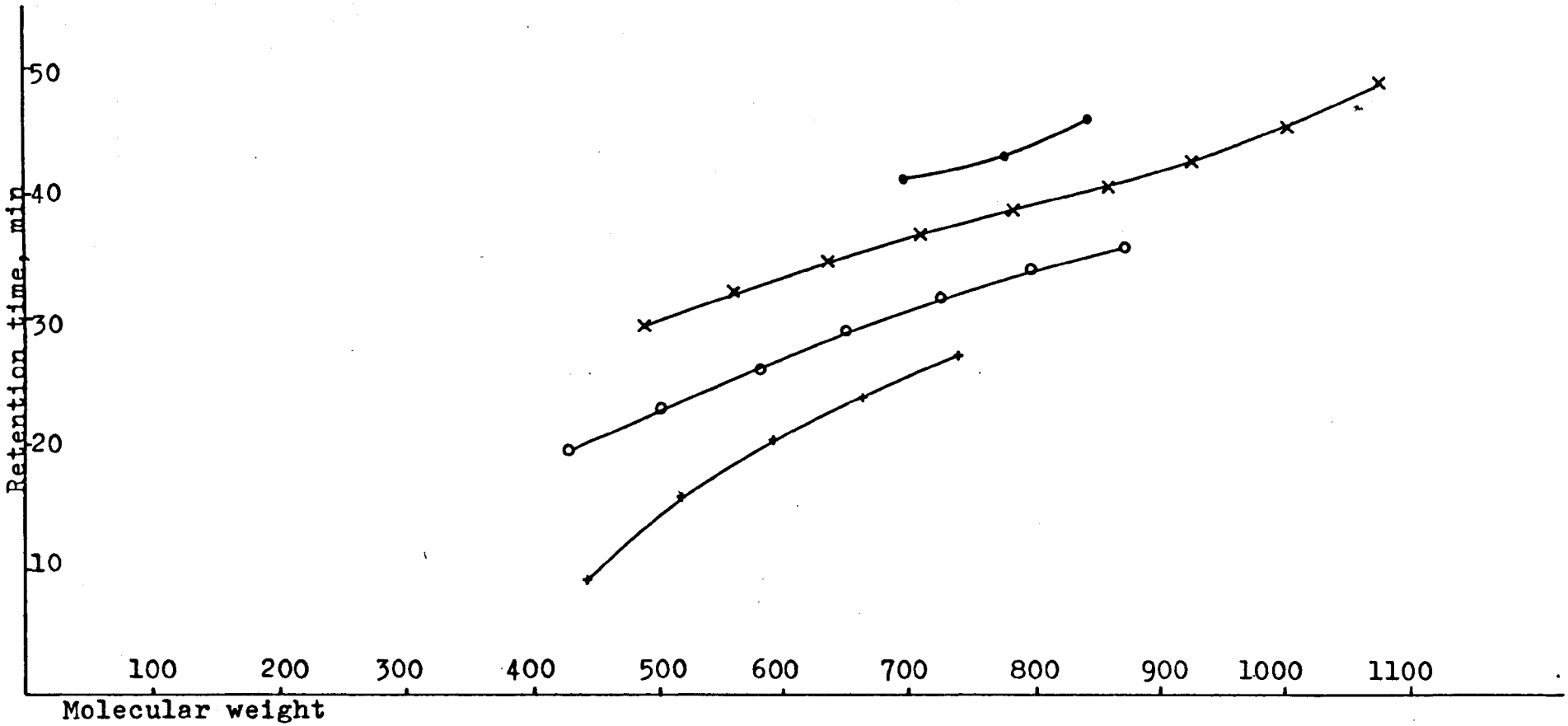


Fig. 4.13(b) Retention time versus molecular weight of the cyclic products of degradation of polymer A heated to 500°. Programme, 5° min^{-1} from 50° to 270°, thereafter held at 270°.

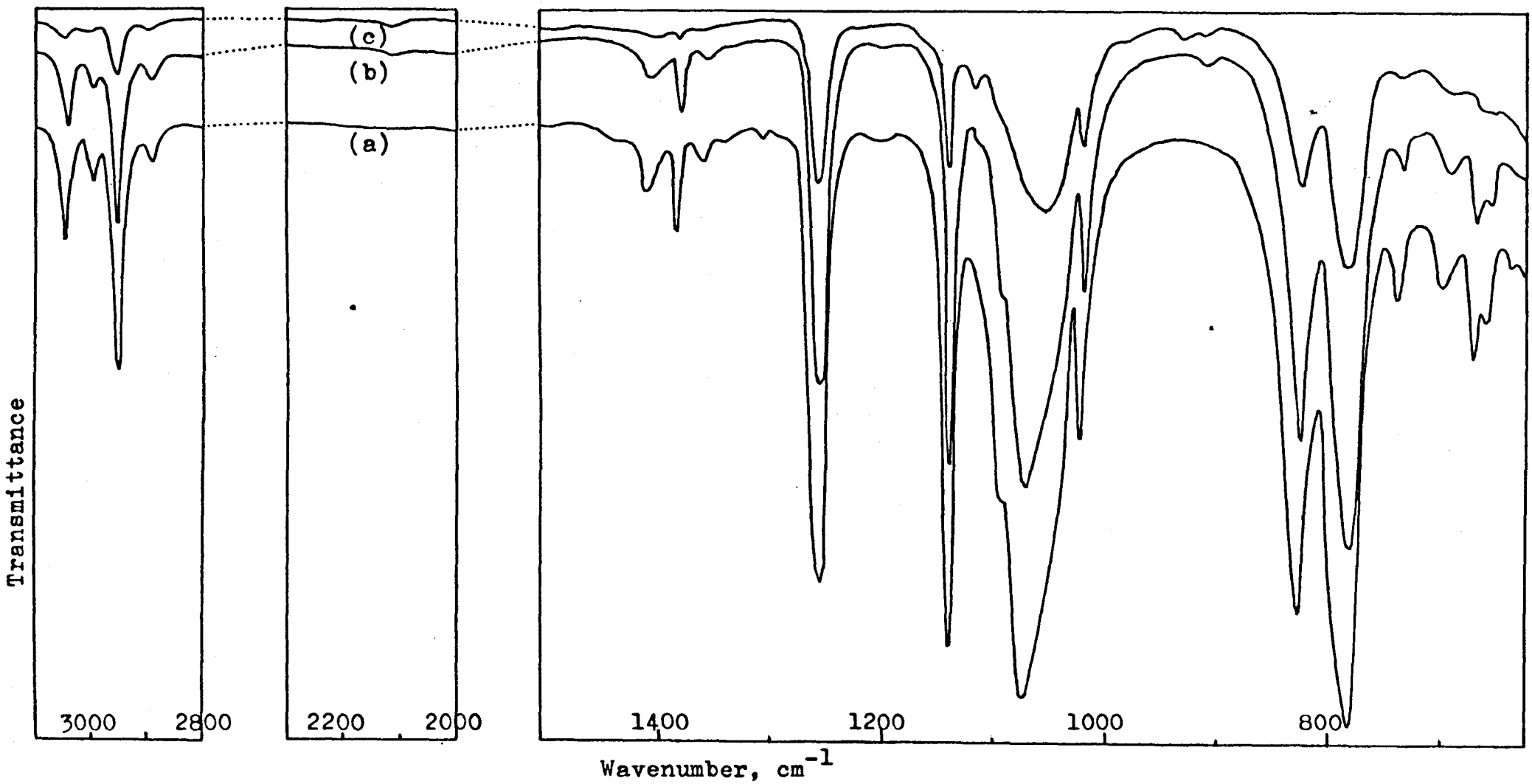


Fig. 4.14 Infrared spectra of the residue from TMPS heated at :(a) 350° and 400°; (b) 450°; (c) 500°.

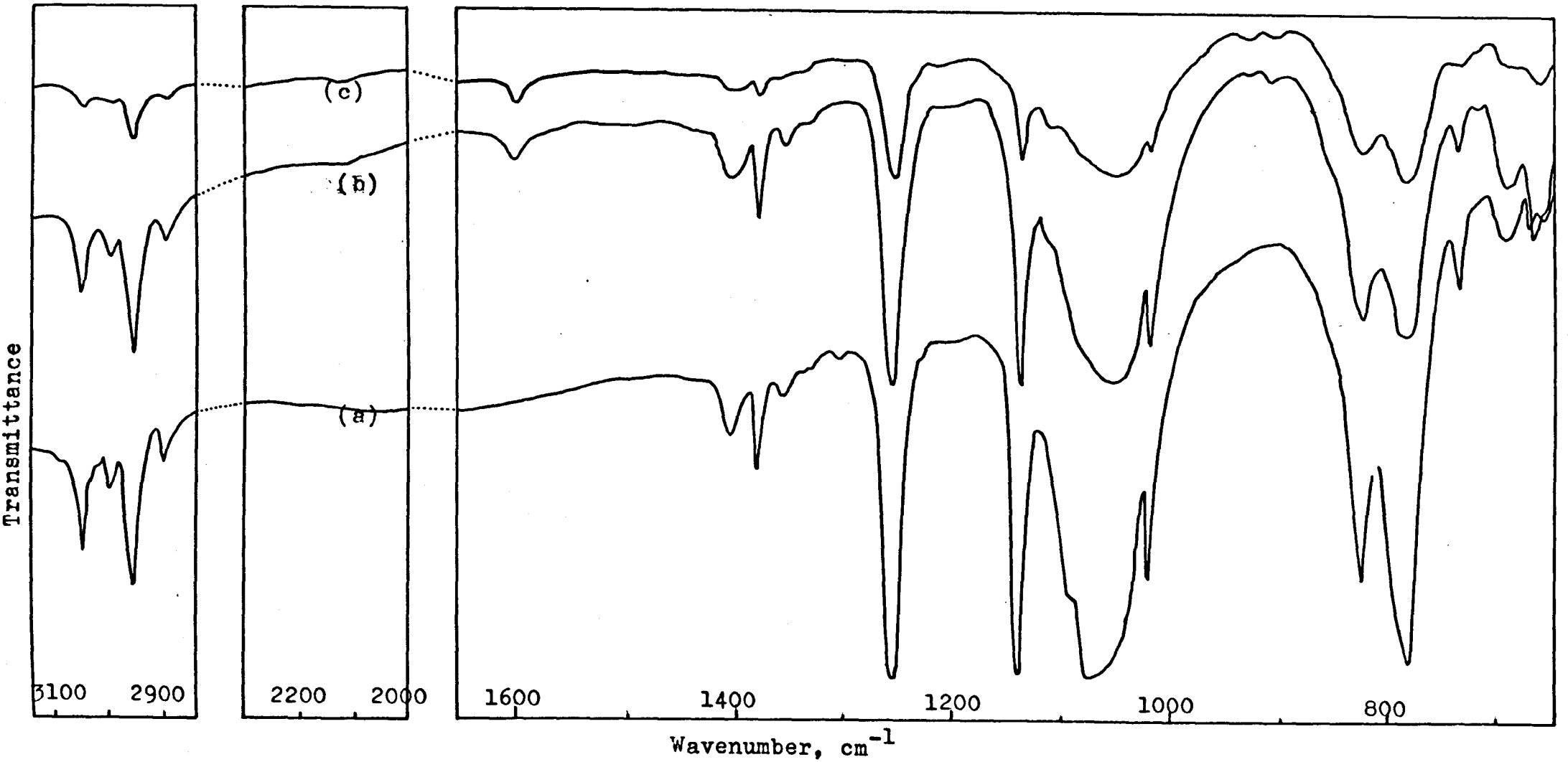


Fig. 4.15 Infrared spectra of the residue from polymer E heated at :(a) 350° and 400°; (b) 450°; (c) 500°.

C and D where the numbers of silphenylene-siloxane units and of siloxane units are nearly equal and was absent when TMPS degrades.

Molecular weight measurement

The number average molecular weights, Mn, of the residues after degrading over a wide temperature range for various periods of time were measured. When the p-phenylene content was low a slight rise in Mn was observed before gel formation prevented subsequent measurements. This is illustrated in Figure 4.16 for polymer B. The graphs of Mn versus time for polymer C and TMPS are plotted in Figures 4.17 and 4.18 respectively. Here no change in Mn was observed. Further increase in temperature results in gel formation so that Mn can no longer be obtained by membrane osmometry.

Sol-gel analysis

Charlesby and Pinner (Ref 28) played a significant part in developing the theory relating the soluble fraction of a degraded polymer residue to the rates of simultaneous chain scission and crosslinking. Although this relation is valid in thermal degradation studies, it has been applied mainly to photolysis reactions. Several equations were derived by Charlesby and Pinner in their original paper (Ref 28) relating the sol fraction (S) to the time (t) of heating or irradiation. The one most suited to this work involves the rates of chain scission (p_o) and crosslinking ($q_o/2$) per monomeric unit and the number average chain length (u).

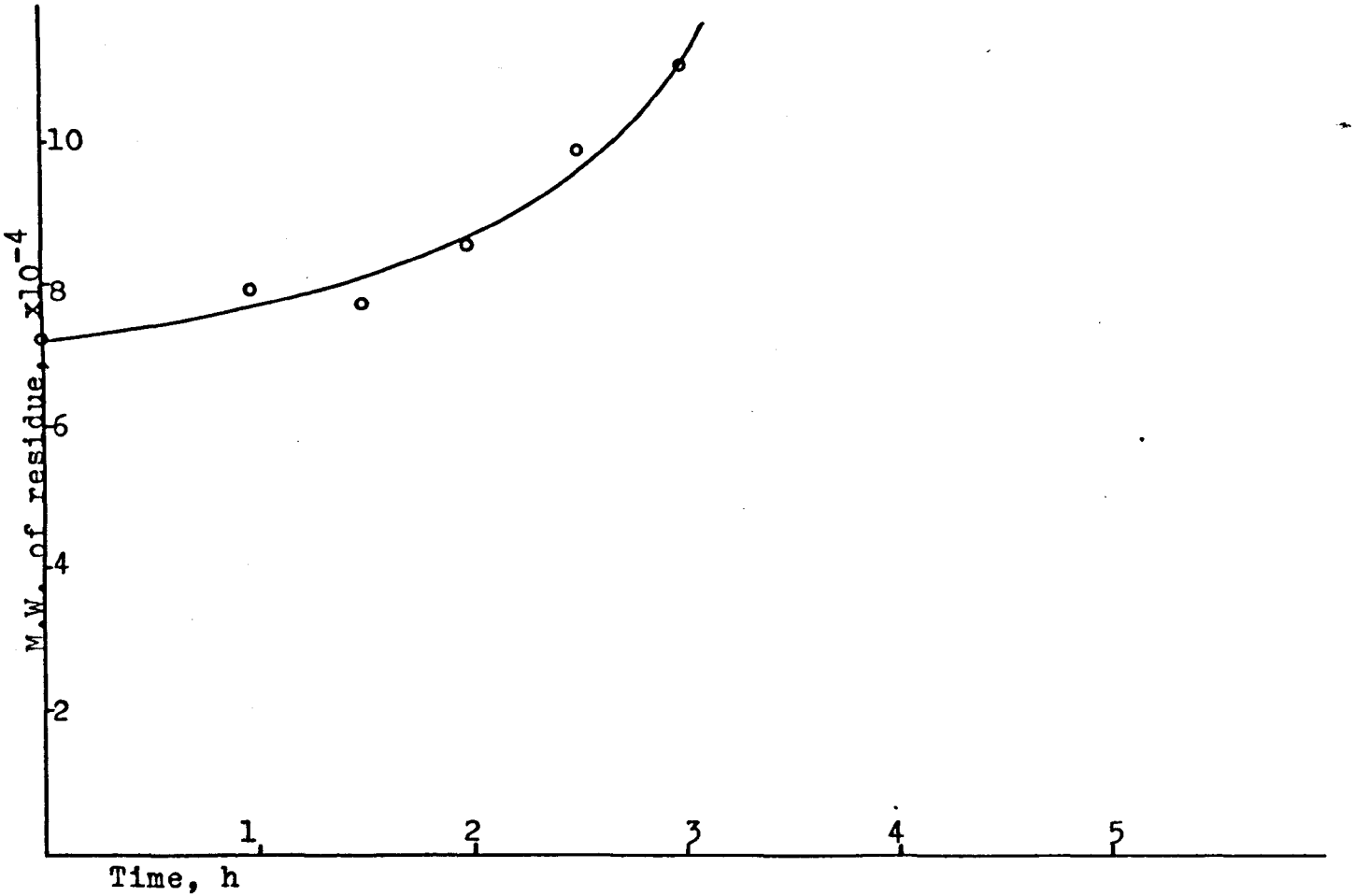


Fig. 4.16 Molecular weight changes in polymer B when heated at 250°.

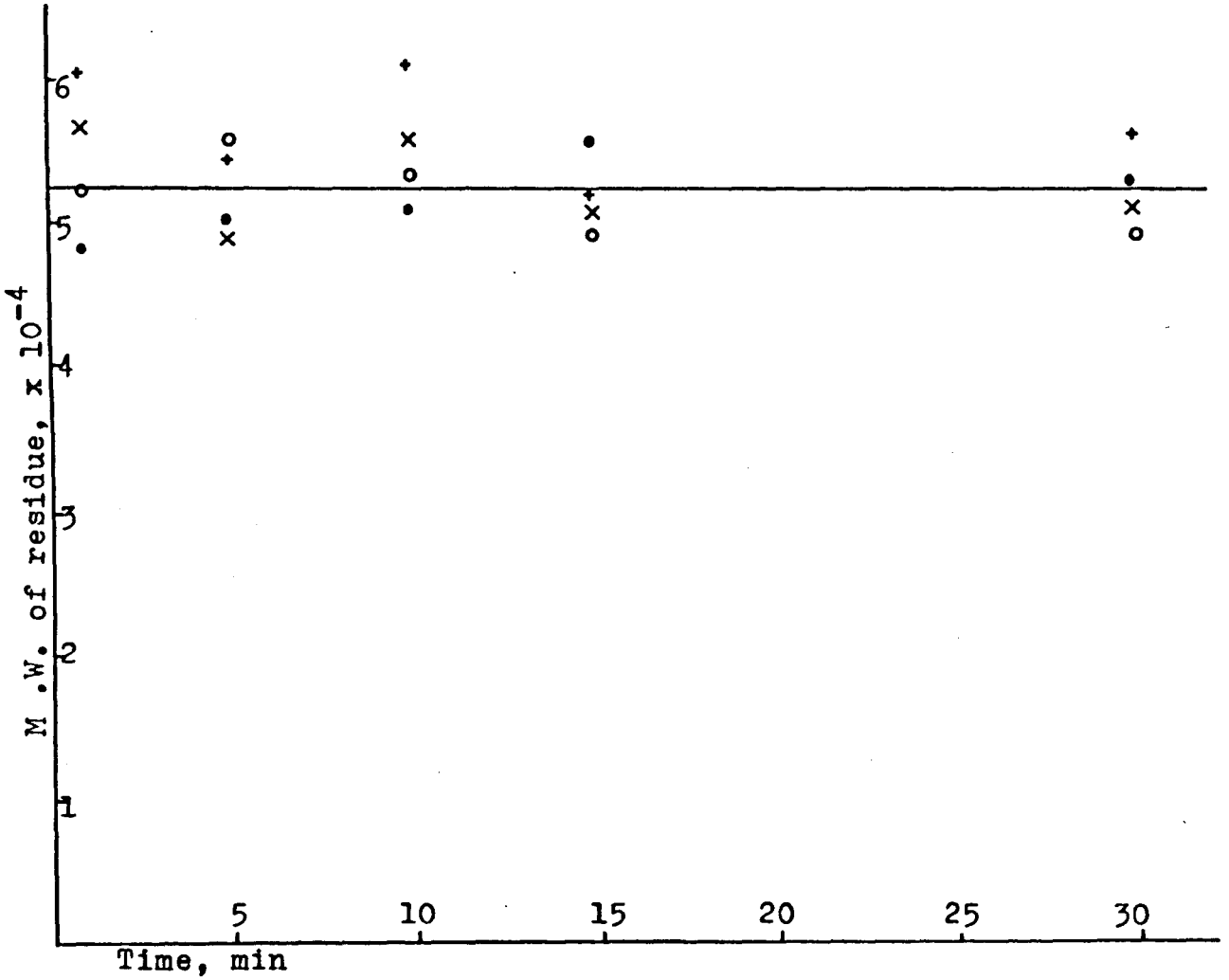


Fig. 4.17 Effect of temperature on the molecular weight of polymer C.
o 150°; x 200°; • 250°; + 300°.

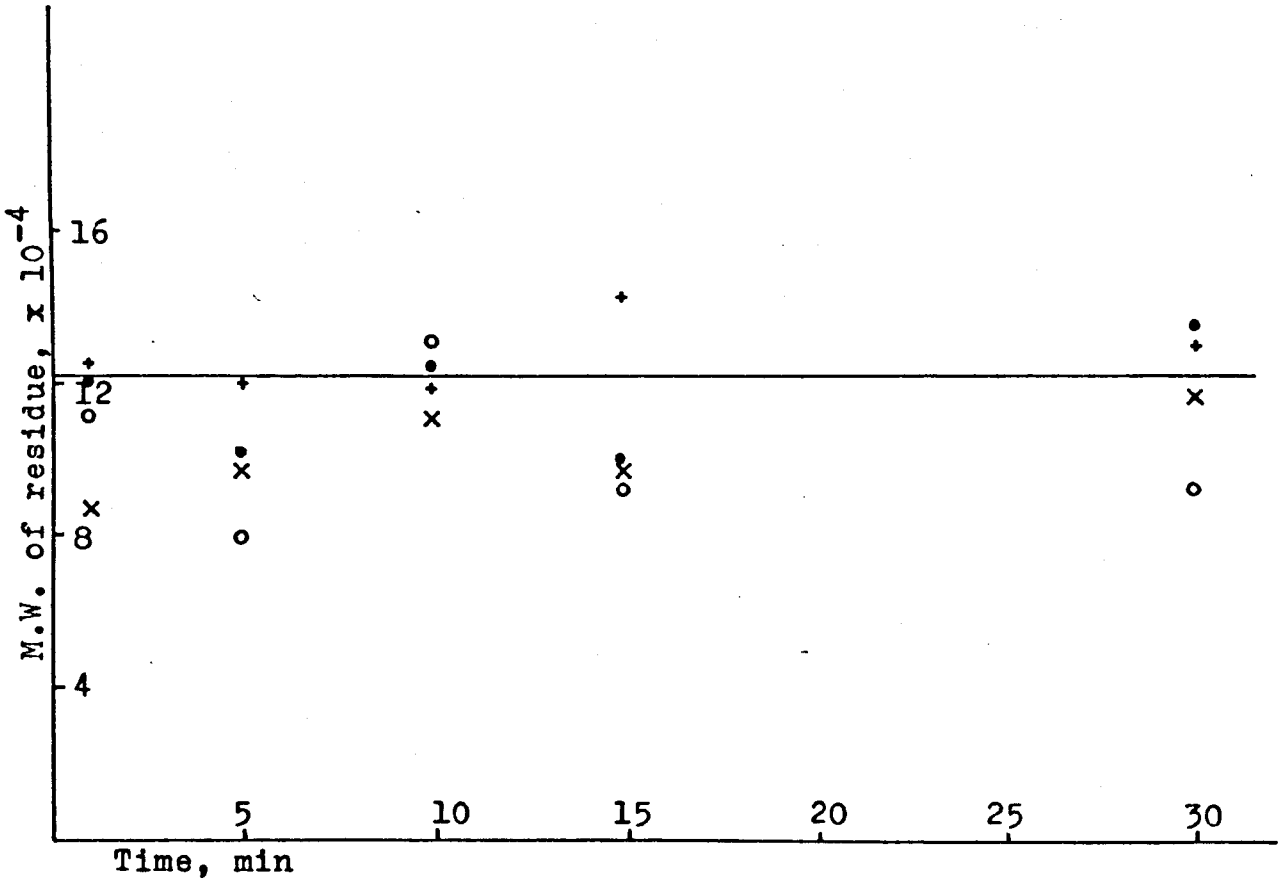


Fig. 4.18 Effect of temperature on the molecular weight of TMPS.
o 150°; x 200°; • 250°; + 300°.

$$S + \sqrt{S} = p_o/q_o + \frac{1}{q_o ut} \qquad A$$

Heating TMPS or one of the copolymers under vacuum at 350° or 400° introduces an insoluble or gel fraction in the residue. The time intervals were varied and the sol fraction noted. Plots of $S + \sqrt{S}$ against 1/t were linear (Figures 4.19 and 4.20) as predicted by equation A. The lines were obtained by the method of least squares and p_o and q_o calculated.

In the original mathematical derivation, Charlesby and Pinner considered scission and crosslinking to occur consecutively rather than simultaneously. No allowance was made for volatolization. At 400° TMPS and each of the TMPS/DMS copolymers underwent simultaneous scission, crosslinking and volatolization rendering the absolute value of the rates calculated from equation A unreliable. However these rate values are of interest relatively since they allow useful comparisons to be made as in Figures 4.21 and 4.22.

In the absence of gel formation the rate of scission may be derived from the equation:

$$N = \frac{1}{CL_t} - \frac{1}{CL_o}$$

where N is the number of scissions per monomeric unit and CL_o and CL_t are the number average chain lengths at zero time and time t. Molecular weight measurements by Grassie and Macfarlane (Ref 3) confirmed that DMS degrades in a stepwise manner to produce volatile cyclic oligomers when heated under similar conditions. For this reason the above equation was considered inapplicable to the DMS depolymerization.

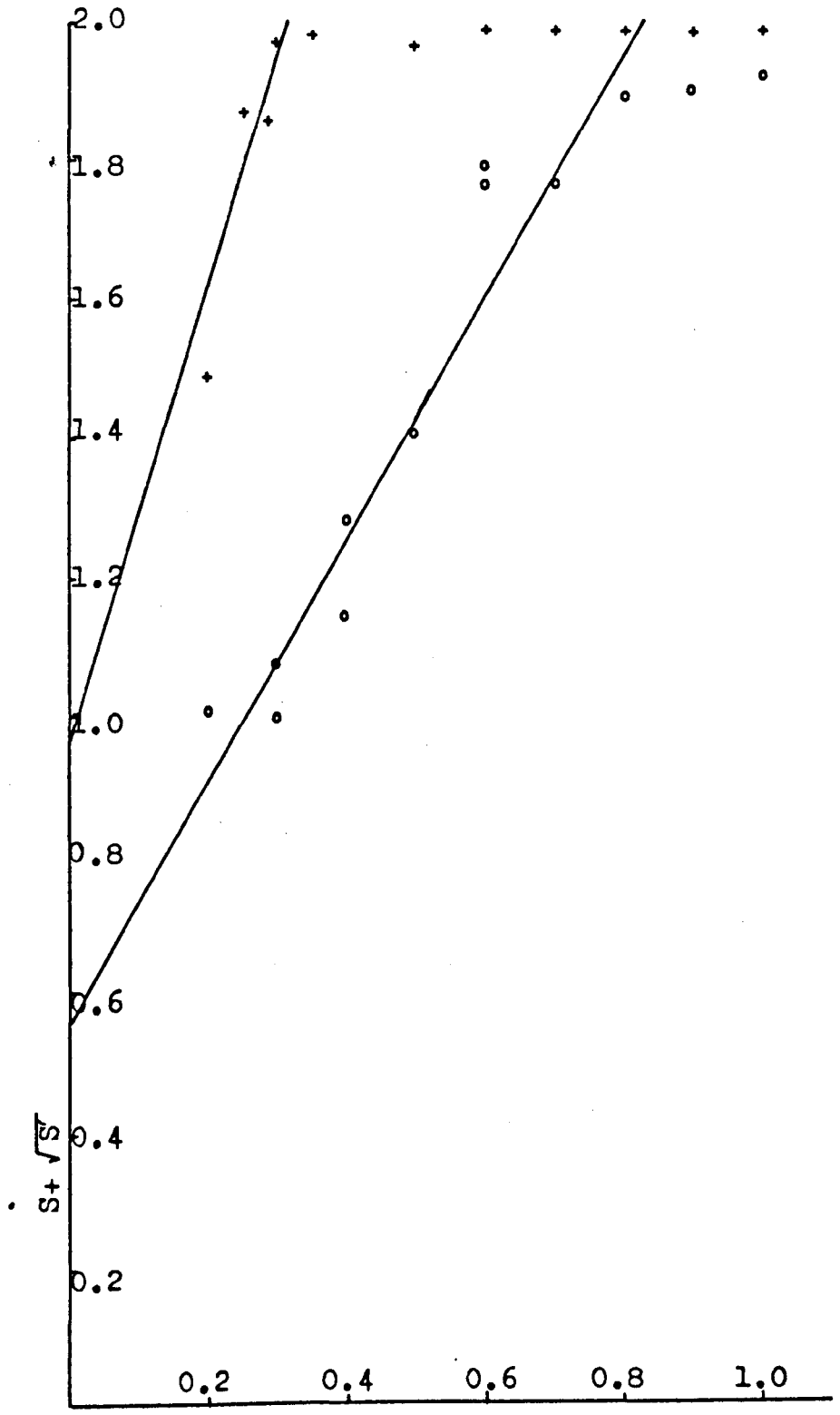


Fig. 4.19(a) Plot of $S+\sqrt{S}$ against 1/t after prolonged heating at 350°.

+ polymer A; ∘ polymer B.

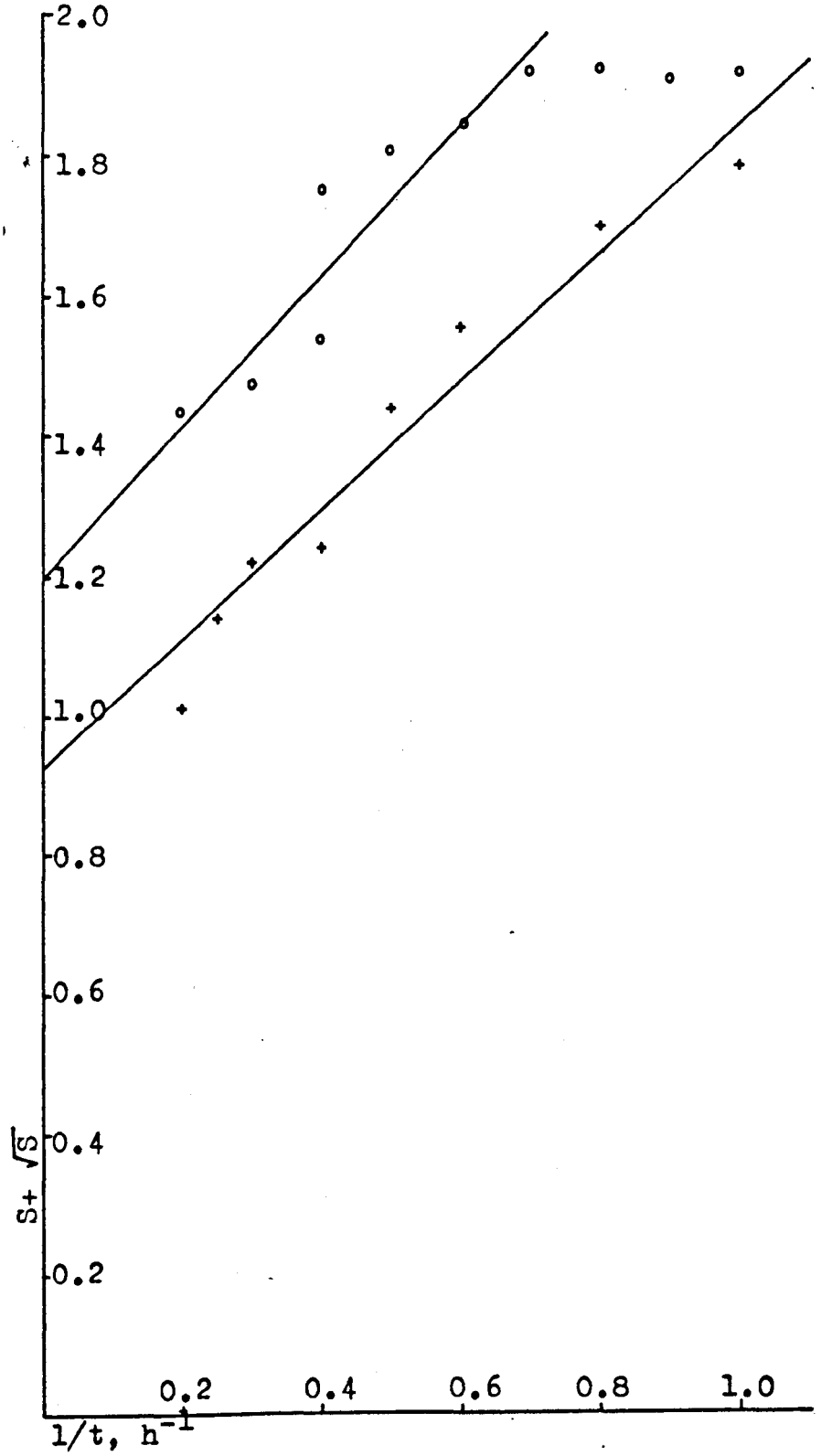


Fig. 4.19(b) Plot of S+ $\sqrt{S}$ against 1/t after prolonged heating at 350°.

+ TMPS; ∘ polymer D.

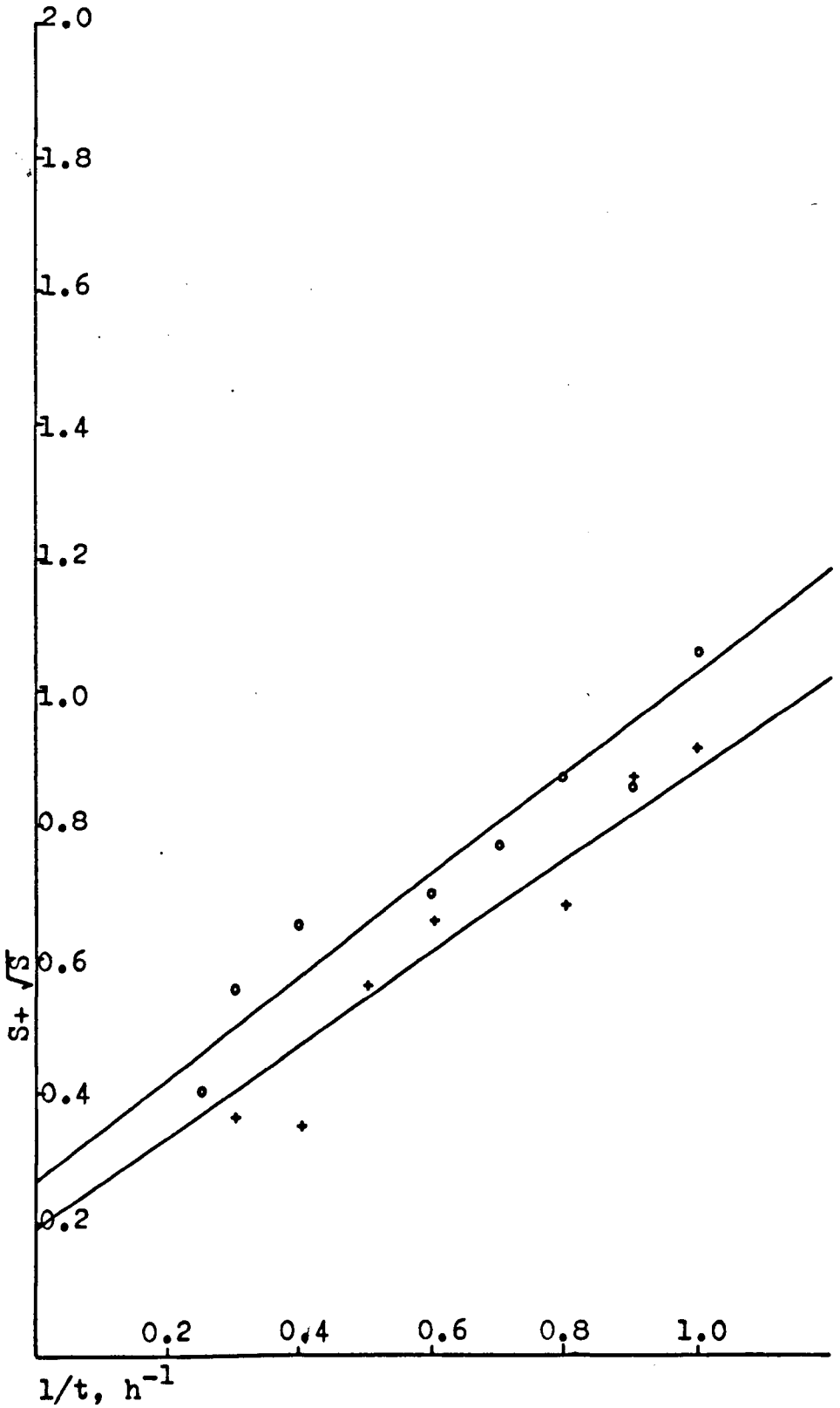


Fig. 4.20(a) Plot of S+ $\sqrt{S}$ against 1/t after prolonged heating at 400°.

+ polymer A; o polymer B.

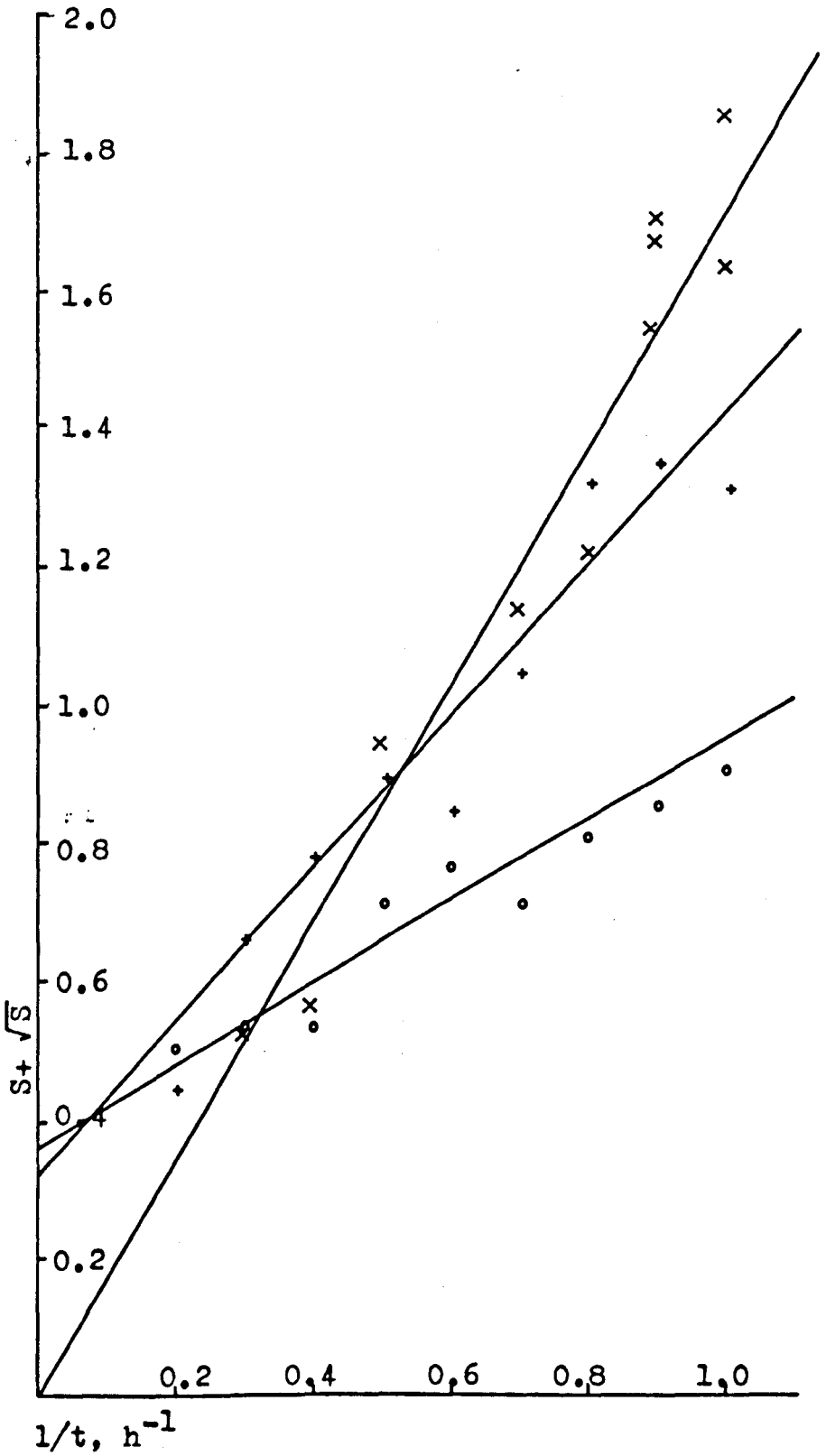


Fig. 4.20(b) Plot of S+ $\sqrt{S}$ against 1/t after prolonged heating at 400°.

+ polymer C; ∘ polymer D; × polymer E.

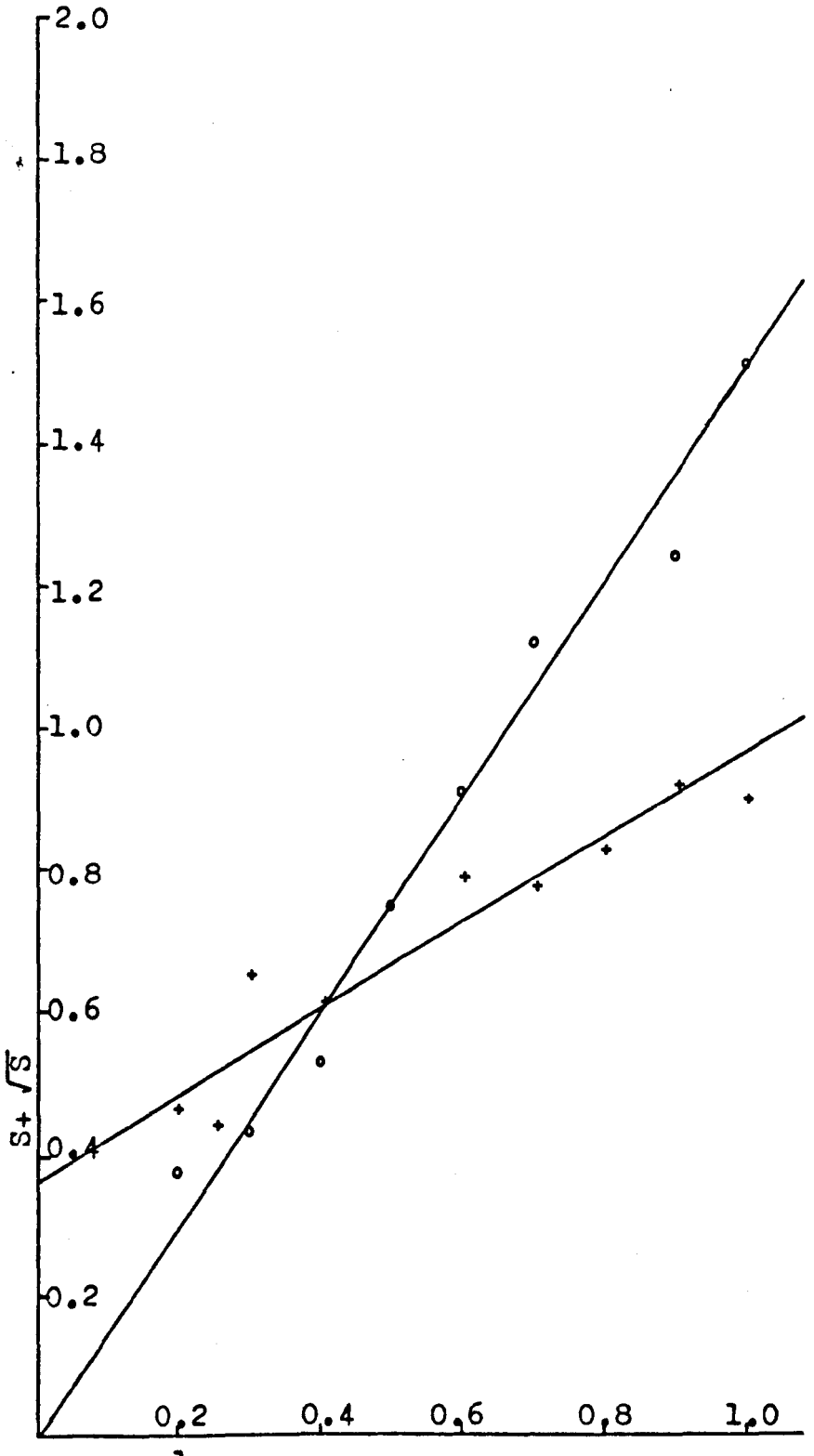


Fig. 4.20(c) Plot of $S+\sqrt{S}$ against 1/t after prolonged heating at 400°.

+ TMPS; ∘ polymer F.

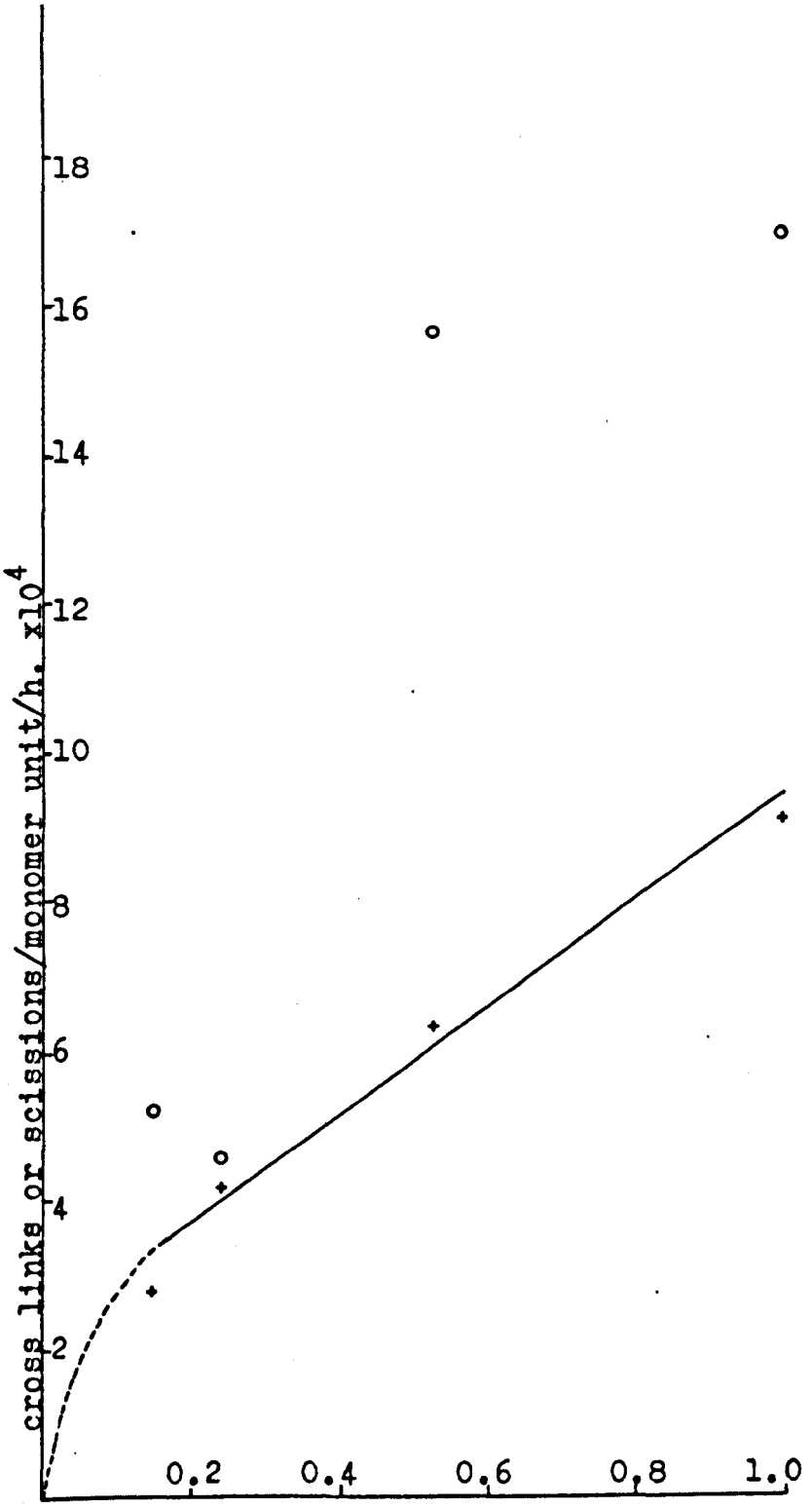


Fig. 4.21 Effect of copolymer composition on rates of cross linking and chain scission when heated isothermally at 350°.
o scission; + cross linking.

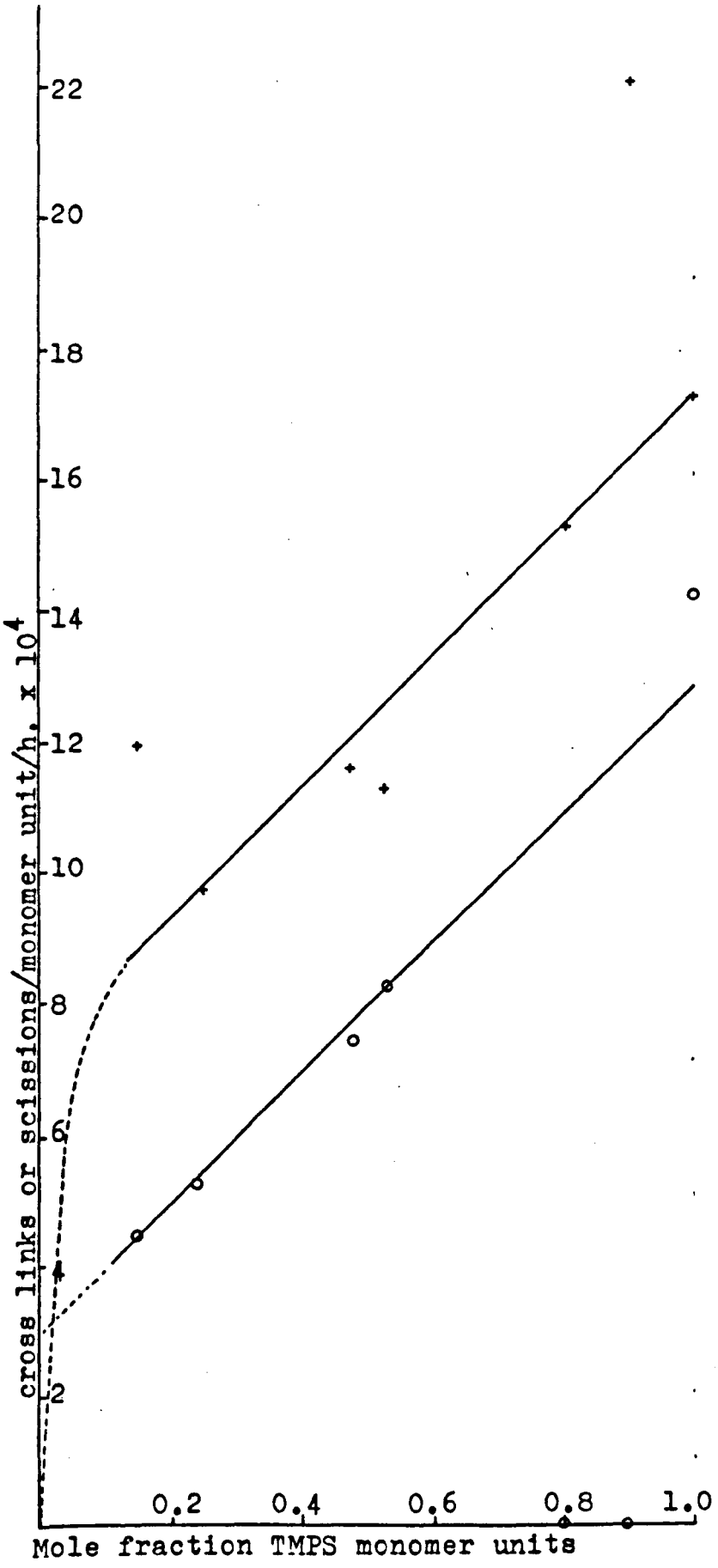


Fig. 4.22 Effect of copolymer composition on rates of cross linking and chain scission when heated isothermally at 400°.
o scission; + cross linking.

Crosslinking, which was absent in DMS, became evident when the p-phenylene group was introduced into the polymer backbone. After an initial rapid rise in rate, the rate increase was essentially linear as the copolymer composition move towards that of TMPS. In all cases the rate was greater at 400° than at 350°. Several polymers remained soluble at 350° so that no rate measurements could be made.

At 350° the rate of scission increased with increasing p-phenylene content but in a rather indefinite manner. When the temperature was raised to 400° the rate was found to vary in an almost linear manner with compostion, although some discrepancies were observed.

Despite there being some doubt as to the quantitative validity of these experimentally derived rate values, sol-gel analysis has demonstrated the qualitative effect of the p-phenylene content on the mode of degradation. DMS heated at 350° and 400° degrades in a stepwise fashion to give a soluble residue. The introduction of even a small number of p-phenylene units results in insolubility. As the number of p-phenylene groups increases, the rates of both chain scission and crosslinking increase, reaching maximum values for TMPS. This suggests that both chain scission and crosslinking are either directly or indirectly associated with the p-phenylene group.

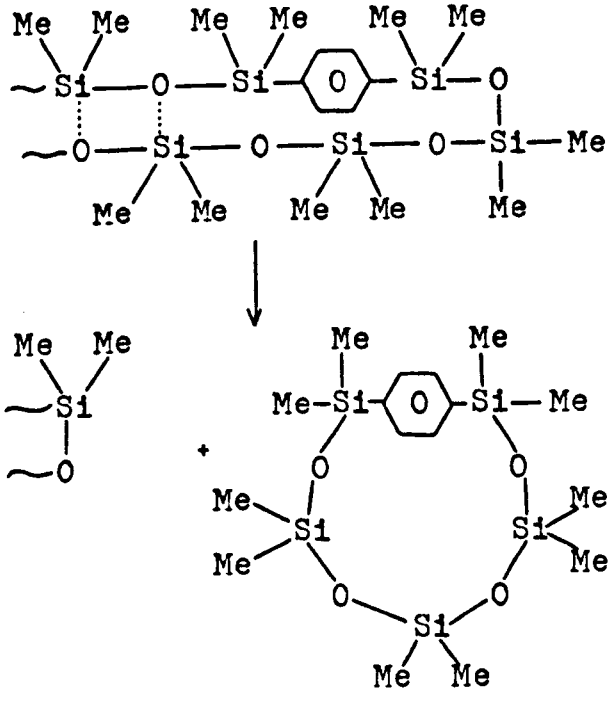
Weight loss measurement

In preparation for sol-gel analysis the polymer samples were degraded at 350° or 400° for periods of up to 5 hours.

The rate of weight loss under these conditions was found to be essentially linear. This is illustrated for polymer D at 350° and 400° in Figure 4.23. The influence of the copolymer composition on the rate of weight loss is shown in Figure 4.24. Introducing a small number of p-phenylene units in place of oxygen atoms into the polymer backbone gave a marked reduction in rate. Thereafter a further increase in the p-phenylene content had little effect.

4.4. Discussion

In common with many inorganic polymers, TMPS and the TMPS/DMS copolymers appear to undergo rearrangement reactions when heated under vacuum. At the lower temperatures of degradation, 350°-400°, the cyclic dimethylsiloxane trimer and tetramer are evolved in every case. Increasing the siloxane content in the copolymer results in an increase in the range of cyclic oligomers produced. To account for these cyclics a mechanism similar to that invoked by Thomas and Kendrick for the decomposition of DMS (Ref 6) is proposed:



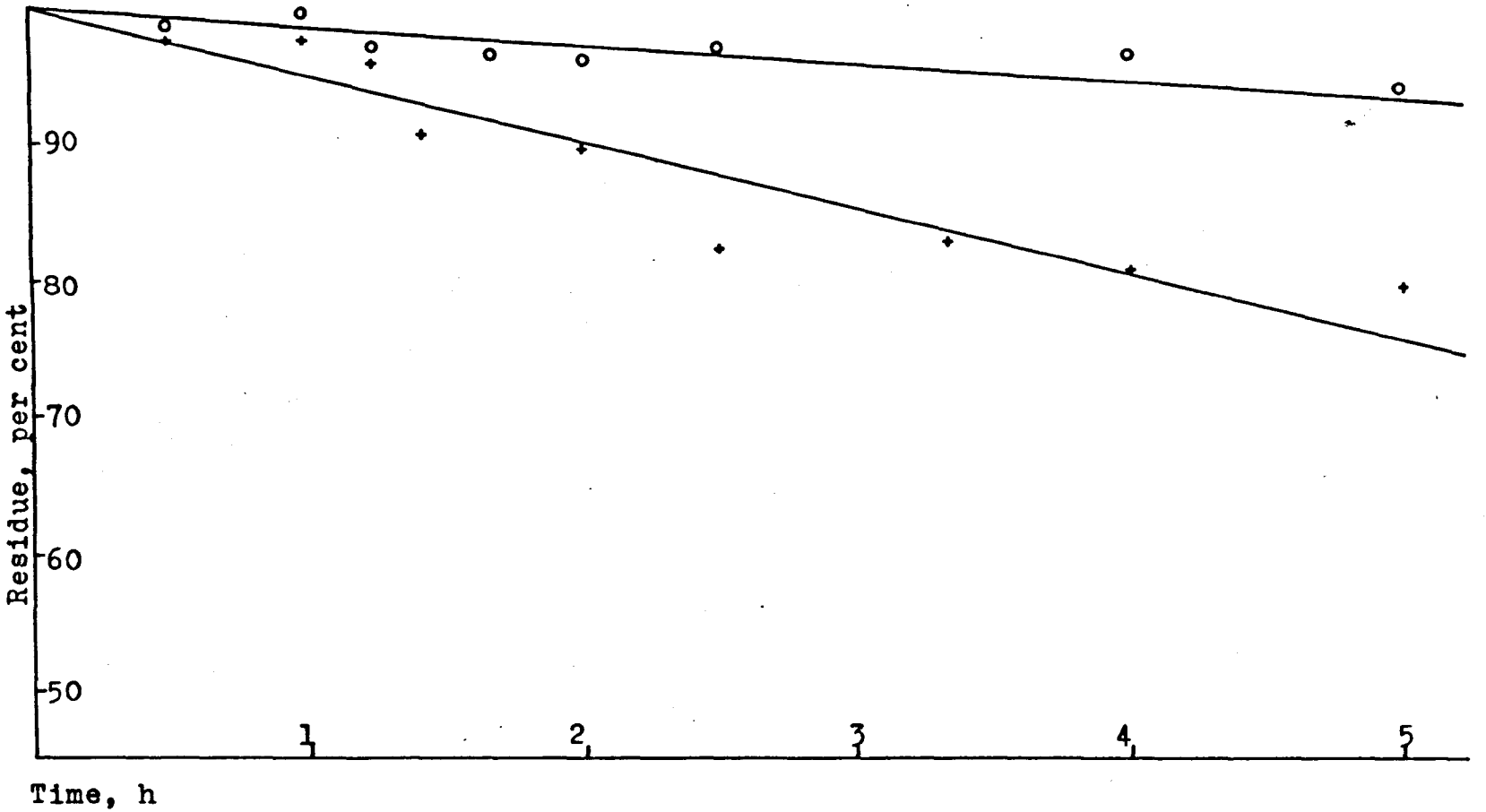


Fig. 4.23 Effect of temperature on isothermal weight loss of polymer D. o 350°; + 400°.

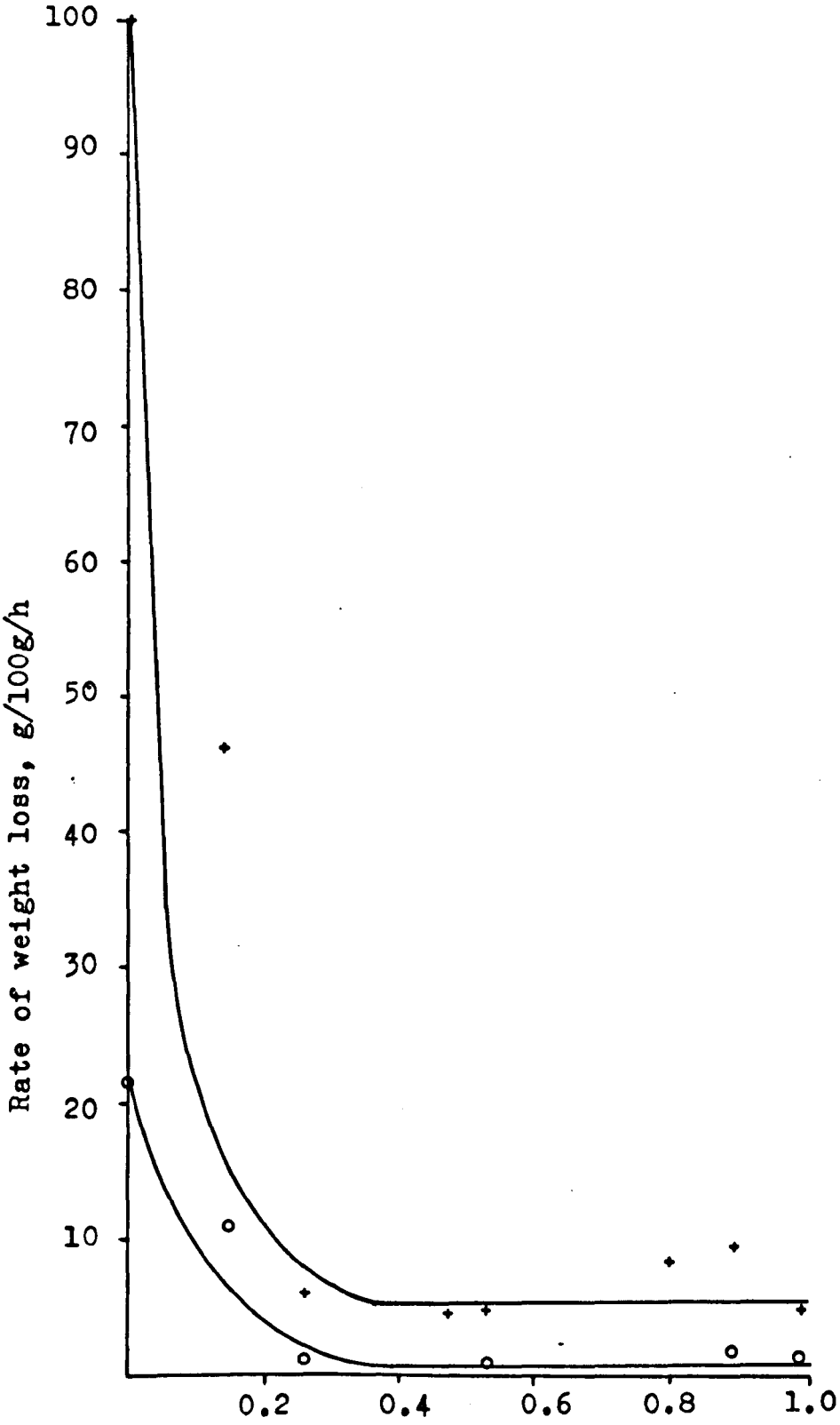
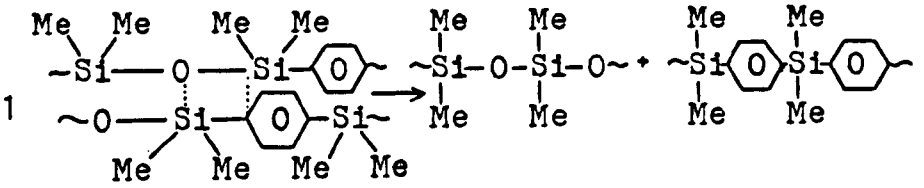
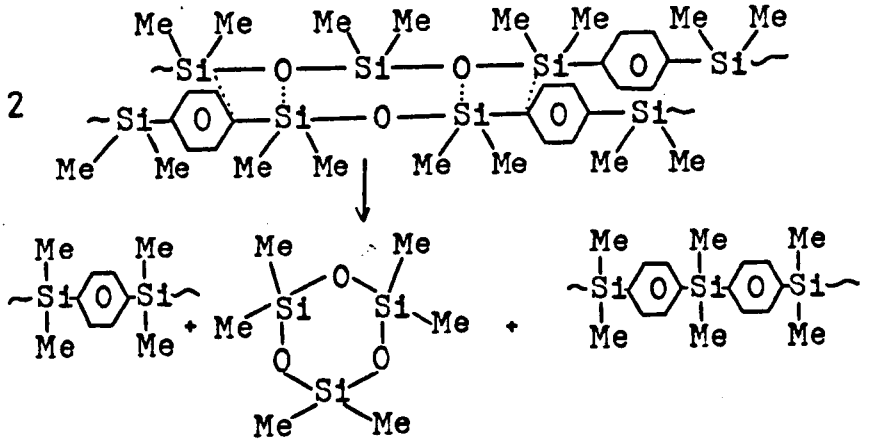


Fig. 4.24 Effect of copolymer composition on the rates of weight loss at 350° and 400°.
o 350°; • 400°.

Nucleophilic attack by oxygen at the silicon leads to the formation of a cyclic transition state. The resulting cyclic oligomer may contain one or more silphenylene groups.

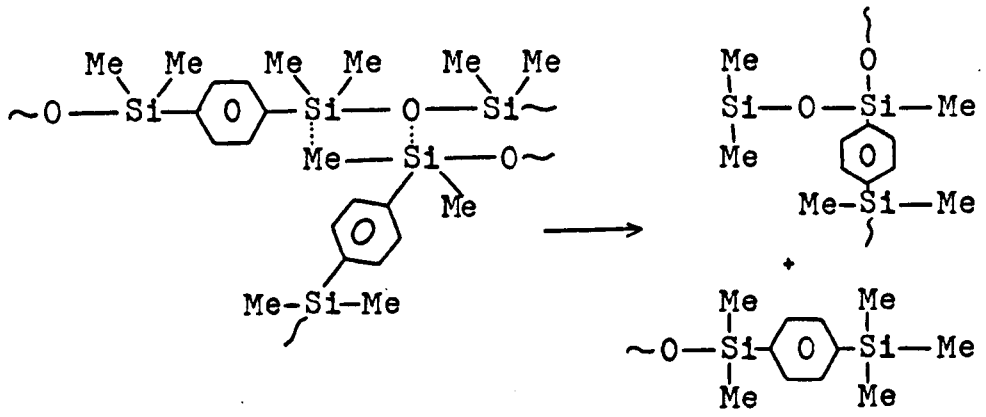
In order to account for the formation of cyclic oligomers in the TMPS degradation an alternative to this intramolecular cyclisation is necessary. The intermolecular rearrangement of siloxane and silphenylene bonds proposed by Zelei at al (Ref 26) would appear to be more valid.





In this mechanism, more than one step may be involved in the formation of one cyclic oligomer.

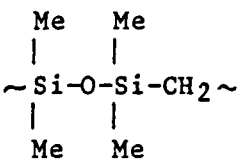
Another feature observed in the degradation of the p-phenylene containing polymers from 350° upwards is the formation of an insoluble fraction in the polymer residue. A mechanism again involving nucleophilic attack by oxygen at silicon is invoked.



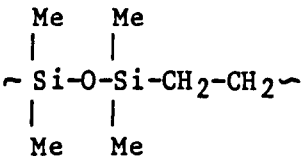
Throughout these structural reorganisations oxygen plays an important part in the formation of the transition state. Thomas and Kendrick (Ref 13) investigated various polysiloxanes with different substituents on silicon and in the main siloxane chain. They found that for polysiloxanes of the general formula $\sim R_1R_2SiO\sim$ a plot of the Taft constant (σ^*), which measures the ability of the substituent on the silicon atom to accept or donate electrons, versus the calculated activation energy of depolymerization was linear. This suggested that the activation energy is a function of the electronic effect of the group attached to the silicon. The value of σ^* used for the phenyl group was -0.10 (Ref 46) and not +0.60 as is usually quoted when it is attached to other atoms or groups. The difference in the values of the Taft constant is due to the availability of vacant d orbitals on silicon to act as acceptors in $d\pi - p\pi$ interactions (Ref 14). This back donation of electrons renders the phenyl group slightly electron donating (negative σ^*) instead of electron withdrawing

(positive σ^*) as in other systems.

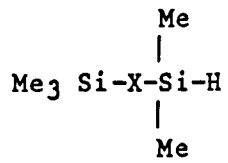
When they studied the degadation of poly (tetramethylsilmethylene-siloxane)



and poly(tetramethylsilethylene-siloxane)



Thomas and Kendrick (Ref 13) calculated the activation energies to be 30 ± 3 and 27 ± 3 kcal mol^{-1} respectively, both being lower than the 43 ± 3 kcal mol^{-1} calculated for DMS (Ref 6). This was attributed to the electron donating effect of the methylene and ethylene groups increasing the electron density on oxygen. Values of the Si-H stretching frequency in compounds

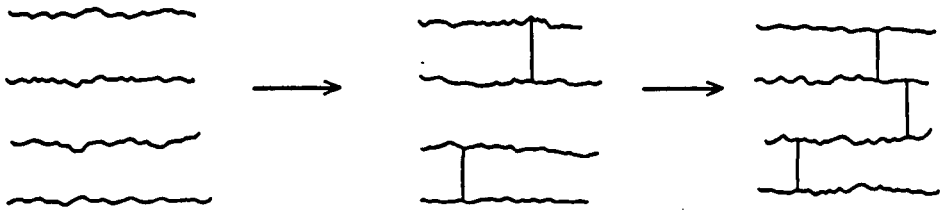


where X represents CH_2 or O reflected the greater capacity of the methylene group for electron donation, since the lower the frequency, the greater is the electron donating ability. The larger electron donation of the ethylene group leads to the lower activation energy for the silethylene-siloxane polymer.

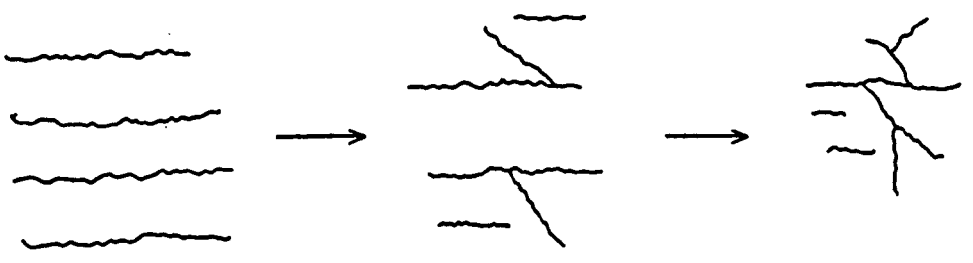
The p-phenylene group, like methylene and ethylene groups, is electron donating when attached to silicon. This in turn increases the electron availability at oxygen which aids

transition state formation with oxygen acting as a nucleophile. Branching occurs instead of cyclic formation due to the inhibitory effect of the p-phenylene group on the chain flexibility.

The above mechanism would suggest that the gel fraction is formed in a chain branching reaction rather than one involving true crosslinking. In a crosslinking reaction, the individual chains join together to give a rapid increase in molecular weight and complete insolubility soon results.

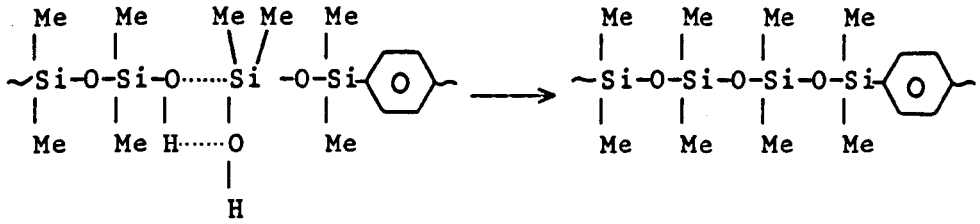


A branching mechanism involves the reaction between two polymer molecules giving one of increased molecular weight and one of decreased molecular weight, thus keeping the average molecular weight constant. If the reaction is purely random, the probability of a molecule reacting further will increase with increasing molecular weight. Therefore although an insoluble fraction is formed complete insolubility will not result.

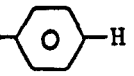


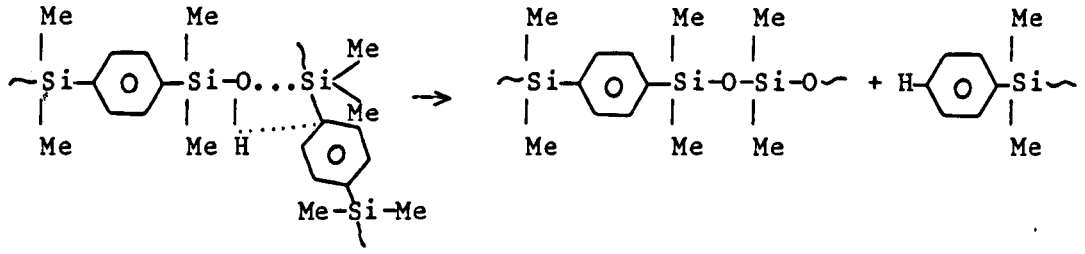
No change was observed in the number average molecular weight in most cases after prolonged isothermal heating which is not unexpected in view of the branching mechanism proposed. Neither did complete insolubility result after 5 hours at 400°. The only exceptions were polymers A and B whose molecular weight did increase prior to the onset of gel formation.

The two polymers which exhibit an increase in molecular weight are those with the highest siloxane content. Thus it would not seem unreasonable to suggest an intermolecular condensation between hydroxyl end groups as in the degradation of DMS.



$+H_2O$

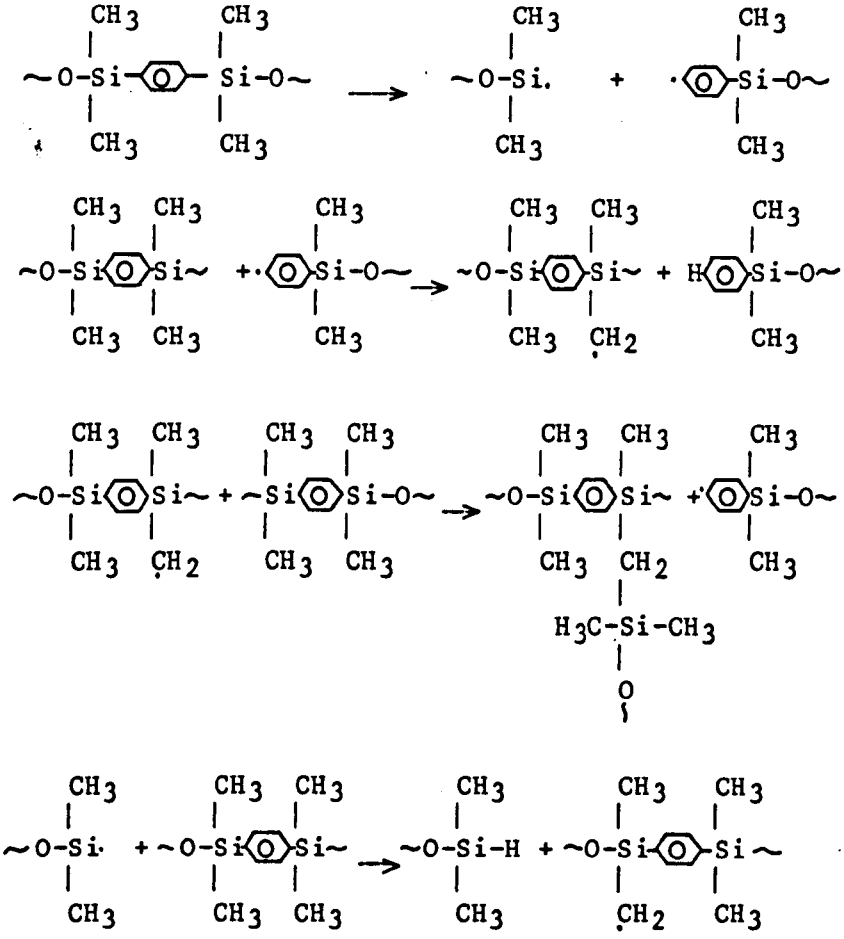
The absence of this reaction in the remaining polymers where the p-phenylene content is greater would imply that the chain ends have been modified. In a recent publicaion (Ref 10) it was reported that hydroxyl end groups in poly(methylphenylsiloxane) assist the cleavage of the Si-Ph bond at temperatures lower than predicted based on the actual bond strength. In the case of the silphenylene-siloxane polymers this would lead to the formation of  end groups in place of the hydroxyl groups:



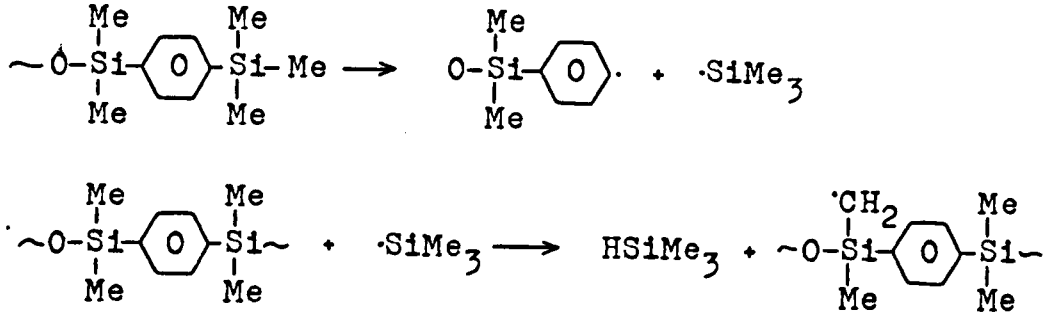
Evidence for the formation of the phenyl end groups is provided by the infrared spectra of both the "cold ring" fraction and the residue.

Thermogravimetry demonstrates that each of the silphenylene copolymers is thermally more stable to weight loss than DMS. This increase in stability may be attributed to both the steric and the electronic effect of the p-phenylene group in the polymer backbone. The mere presence of the bulky p-phenylene group reduces the chain flexibility which in turn hinders the formation of a cyclic transition state. Chain branching results from the electronic effect of the p-phenylene group when it is attached to silicon and will hinder the formation of volatile products.

At higher temperatures the degradation mechanism changes from a structural reorganisation to one involving direct scission of the silphenylene bond. A free radical sequence similar to that proposed by Sobolevskii et al (Ref 16) is suggested.



The short chain oligomers thus formed will have either Si-H or Si-C$_6$H$_4$-H end groups. Both are observed in the infrared spectra of the products of degradation. To account for the formation of the trimethylsilane, cleavage of the silphenylene bond must occur at a trimethyl silyl group formed in the branching process,



4.5. Summary

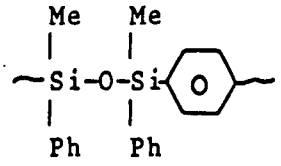
The effect of the introduction of p-silphenylene units into linear DMS increases the thermal resistance to weight loss by hindering cyclic formation and activating the branching reaction. Cyclic oligomers containing both silphenylene and siloxane units and short chain fragments similar in structure to that of the initial polymer are the main products of degradation. At lower degradation temperatures the mechanism may be described as one of rearrangement. This undergoes a change to one involving Si-C bond scission when the temperature is raised. When the siloxane content is low the dominant mechanism involves bond scission and the main products are the short chain oligomers. As the siloxane content is increased the behaviour tends towards that of DMS. Thus there is increasing formation of cyclics and the amount of residue is reduced.

CHAPTER 5

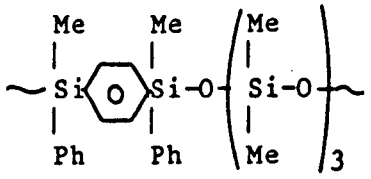
THE THERMAL DEGRADATION OF POLY(METHYLPHENYL-p-SILPHENYLENE-SILOXANE)

5.1. Introduction

Thermal analysis of poly(dimethylsiloxane), DMS, and poly(methylphenylsiloxane) demonstrates that the stability of the siloxane polymer is improved when the methyl substituents are replaced in part by phenyl groups (Ref 3,10). This difference in stability was attributed to the influence of the organic side-group on the degradation mechanism. The presence of aromatic groups within the polymer backbone produces a similar effect (Ref 23). The dimethyl substituted silphenylene-siloxanes are thus more resistant to heat than DMS. An interesting progression would be to investigate the thermal degradation properties of poly(methylphenyl-p-silphenylene-siloxane), MPPS,

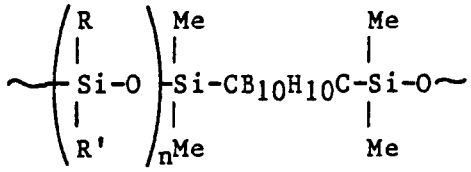


Methylphenyl substituted silphenylene-siloxane polymers have received little attention in the literature. Breed and his co-workers (Ref 23) described the preparation of



from p-phenylenebis(methylphenylsilanol) and a cyclosiloxazane. However no mention was made of either the physical properties or the thermal stability.

Andrianov et al (Ref 47) have studied the thermal breakdown of some di-organocarborane-siloxane polymers,



R, R' = Me,Ph
n = 2,3,4,5,6,80

It is interesting to note the close resemblence of their breakdown pattern to that previously observed in the TMPS/DMS copolymers. In both cases two mechanisms feature in the degradation. One leads to cyclic siloxane oligomers via Si-O bond cleavage while the other proceeds by scission of the Si-C bond to give short chain oligomers. Insolubility also develops in the polymer residue. The overall weight loss of the carborane-siloxane polymers was significantly reduced by replacing several of the methyl groups by phenyl groups. Andrianov explained this by the phenyl group favouring branching or crosslinking which in turn inhibits breakdown of the main chain.

This chapter describes the behaviour of poly(methylphenyl-p-silphenylene-siloxane) when it is subjected to heat. The experimental results are discussed from a mechanistic point of view.

5.2 Thermal analysis

1. TG

The TG curves in Figure 5.1 illustrate the effect of replacing dimethyl by methylphenyl substituted silicon in the silphenylene-siloxane polymer. Both the threshold weight loss temperature and the residual weight are increased by the presence of phenyl groups.

2. DSC

No sharp exotherms or endotherms were observed in the DSC trace (Figure 5.2). However the undulating nature of the trace would suggest that several minor rearrangement reactions take place throughout the degradation process.

3. TVA

An almost negligible rise was detected in the TVA trace for MPPS from which no conclusions were drawn. A second trace was recorded using only two Pirani gauges to detect the presence of gaseous products. The first Pirani gauge was situated between the oven and the trap system to monitor the presence of volatile material as it was formed. The second gauge was situated after the -196° trap and would register only non-condensable products. The trace from the first gauge is illustrated in Figure 5.3. Evolution of gaseous products was detected at 337° reaching a maximum at 370° and from 450° upwards. No non-condensable products were detected. The "cold ring" fraction and the residue constitute the main products of degradation.

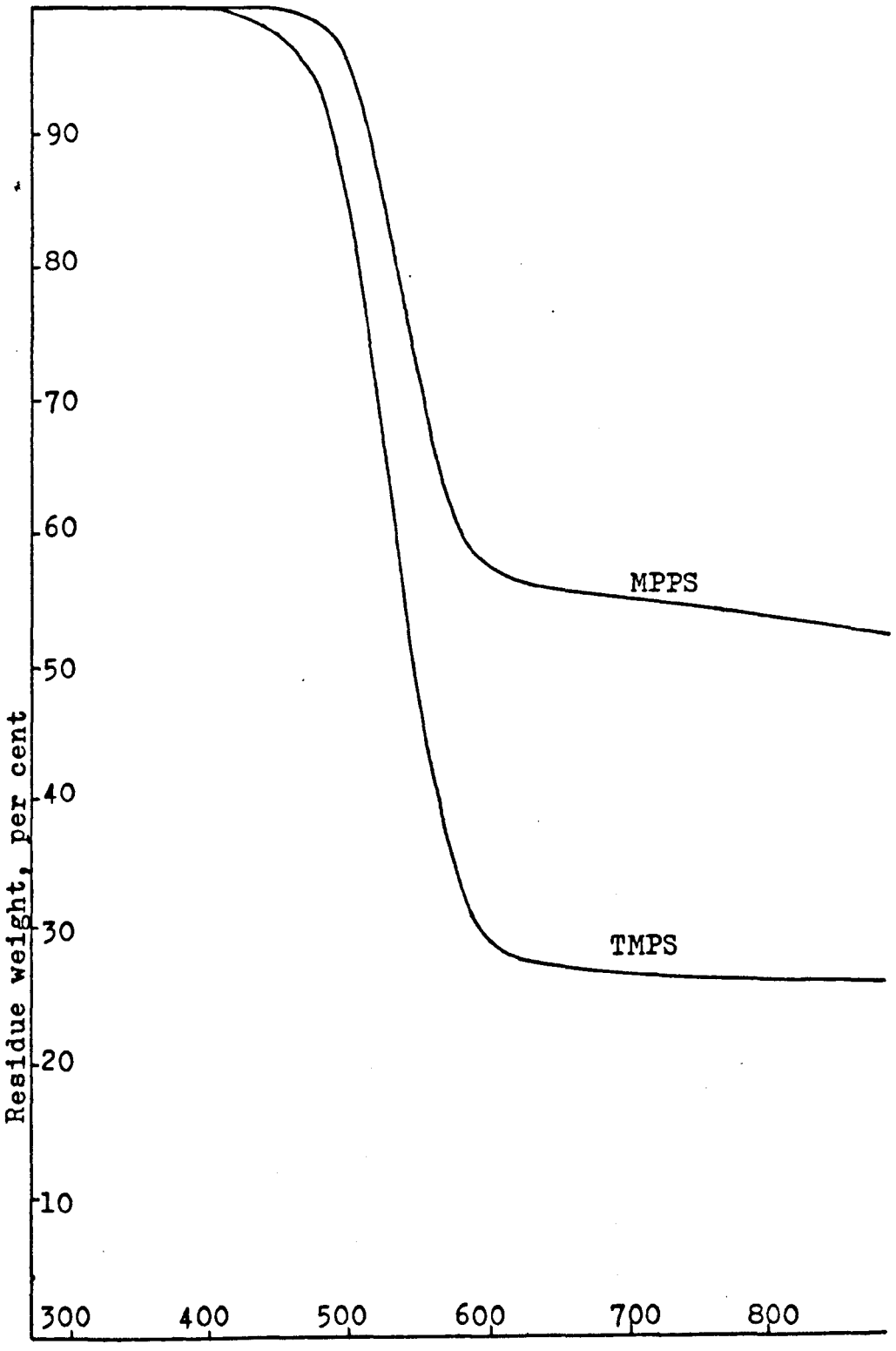


Fig. 5.1 TG of MPPS and TMPS.

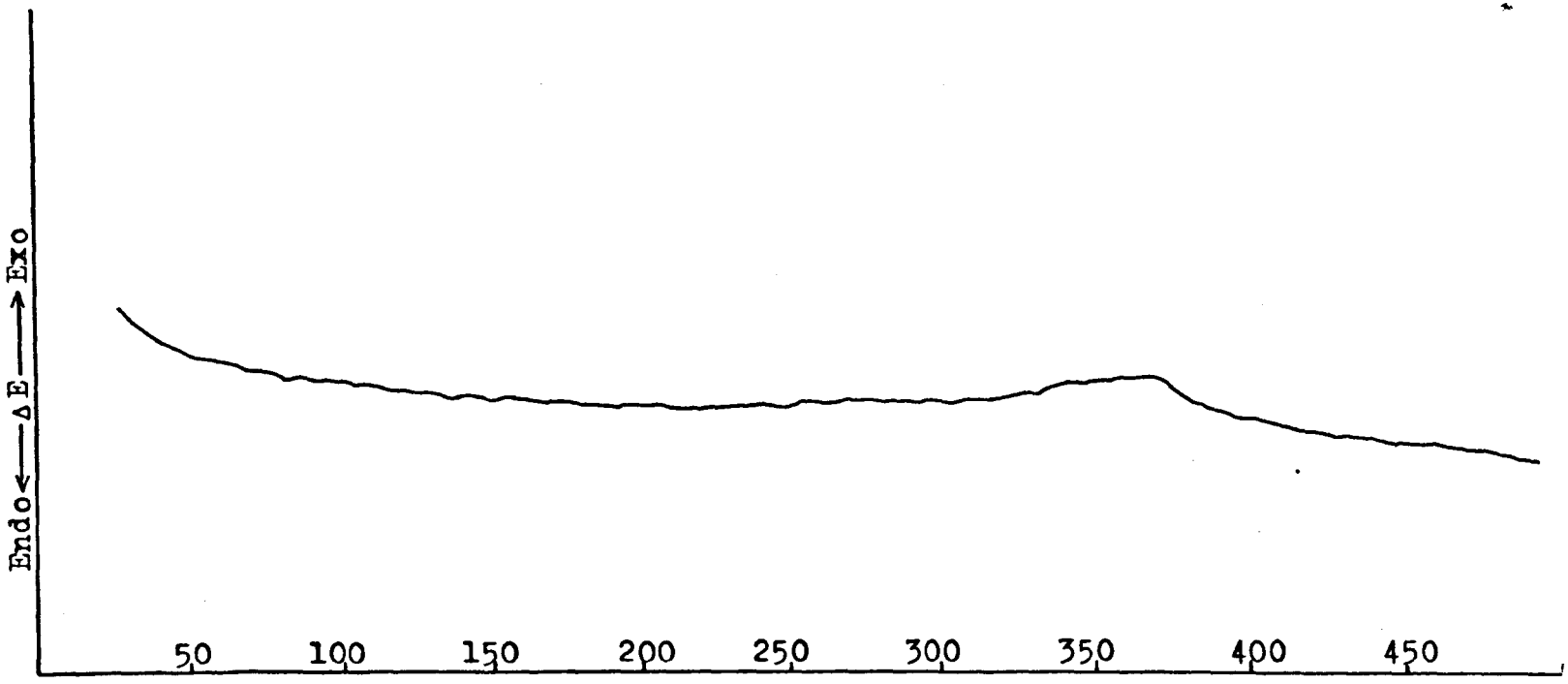


Fig. 5.2 DSC trace of MPPS.

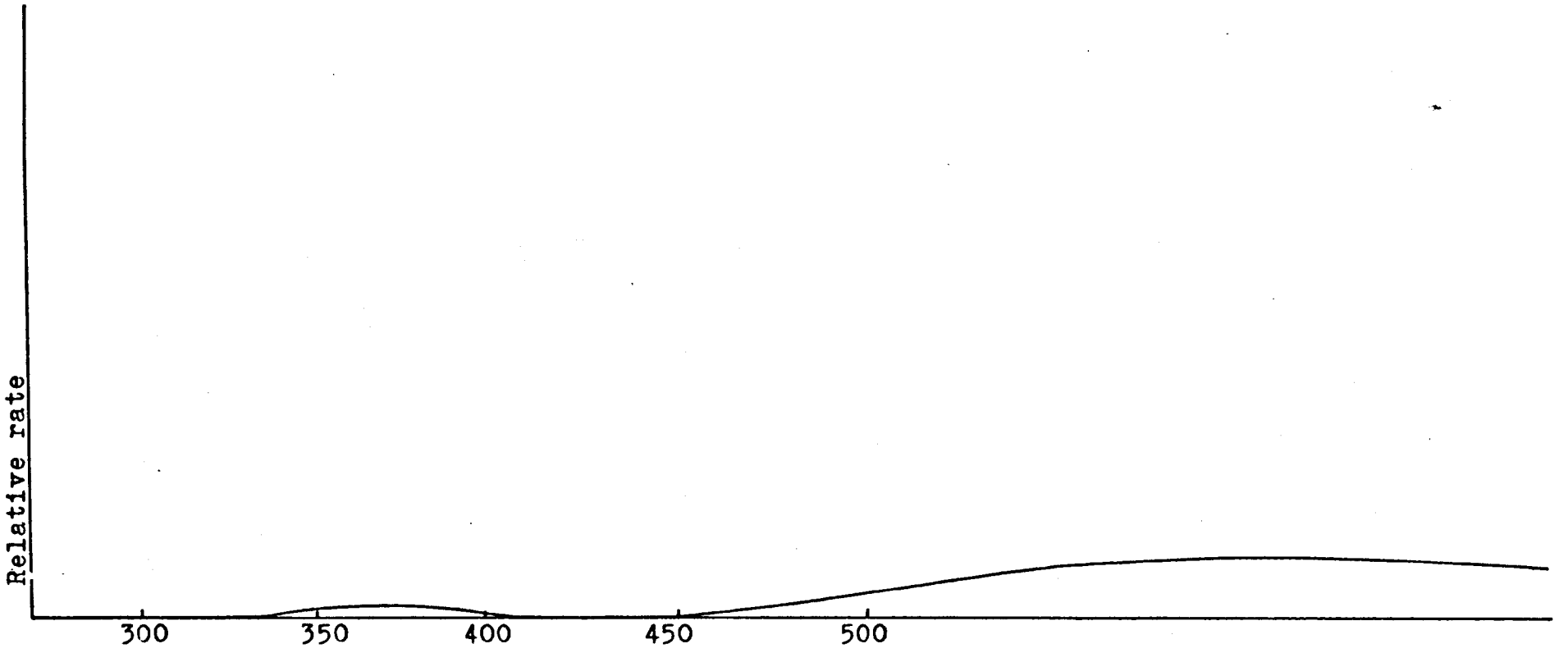


Fig. 5.3 TVA trace for MPPS.
Programme, 10^{o} min^{-1} from ambient to 500^{o}, thereafter held at 500^{o}.

5.3. Analysis of Products from Isothermal Degradation

The range of volatilities of the total products from the isothermal degradation of MPPS conveniently permits their collection in three fractions for further analysis.

1. Condensable products

Infrared analysis

Infrared spectra of the gaseous products from MPPS heated to 390°, 450° and 500° are compared in Figure 5.4. The spectrum of benzene is given in Figure 5.5. Thus benzene was identified as the sole gaseous product at 390°.

At higher temperatures the production of benzene increases and new absorption bands appear at 2960, 2140, 945 and 890 cm^{-1}. These are the characteristic absorptions of the aliphatic C-H (2960 cm^{-1}) and the SiH_3 group (2140, 945 and 890 cm^{-1}) indicating the formation of methylsilane. Comparison of this spectrum with one recorded by Kaye and Tannenbaum (Ref 48) supports this claim.

Ultraviolet analysis

Further evidence of benzene formation was obtained from the ultraviolet spectrum of the gaseous products (Figure 5.6). The absorption maximum at 254 nm, sometimes known as the B-band, is characteristic of benzene.

Mass spectroscopy

Peaks in the mass spectrum of the gaseous material at m/e values of 78, 52, 50 and 39 were observed due to the presence of benzene. An intense peak at m/e 44 corresponds to the $HSiMe^{+}$ ion from $MeSiH_3$. This peak is claimed to be

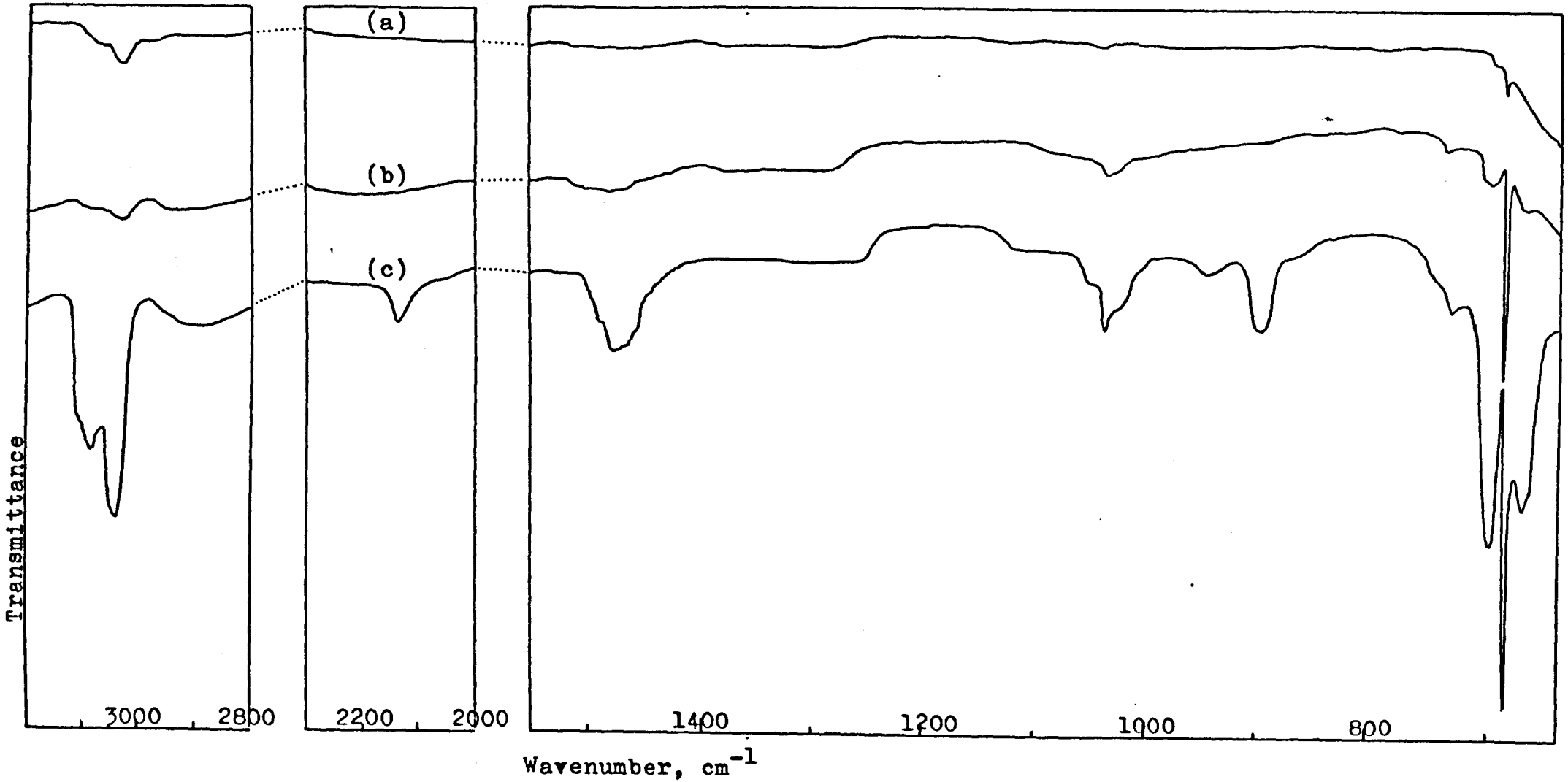


Fig. 5.4 Infrared spectra of the gaseous products from MPPS heated isothermally at: (a) 390°; (b) 450°; (c) 500°.

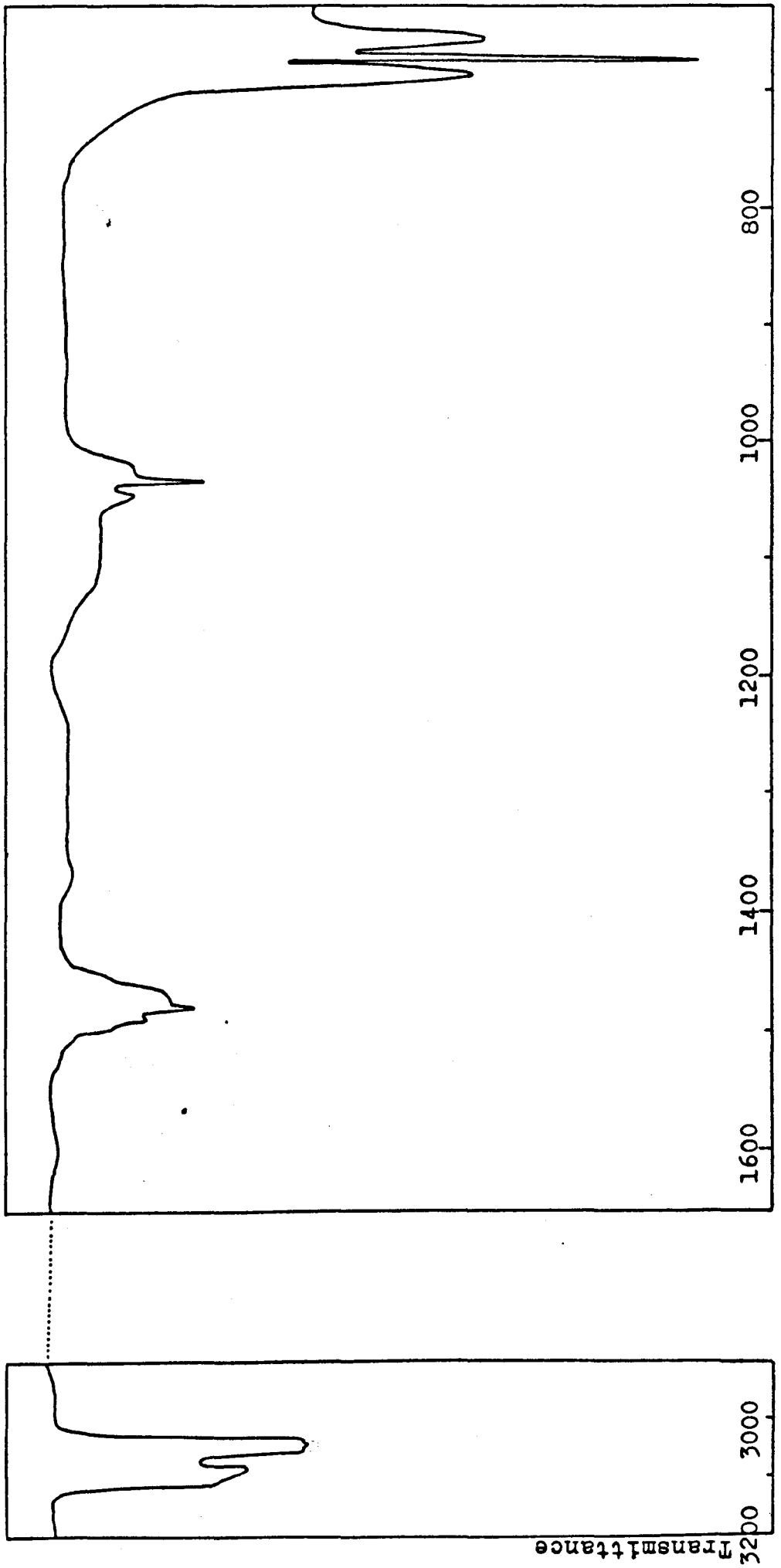


Fig. 5.5 Infrared spectrum of benzene.

the most intense peak in the mass spectrum of methylsilane (Ref 49).

2. "Cold ring" fraction

Infrared analysis

The dependence of the nature of the components in the "cold ring" fraction on the degradation temperature is illustrated in Figure 5.7. After prolonged heating at 400° no difference was detected between the infrared spectra of the "cold ring" fraction and the original polymer. The formation of the Si-H group was indicated by the appearance of new absorption bands at 2120, 920, 885 and 865 cm^{-1} after degrading at higher temperatures. The 950-850 cm^{-1} region is useful for determining the number of hydrogen substituents on silicon. Thus the bands at 920 and 865 cm^{-1} characterise the SiH_2 while that at 885 cm^{-1} results from the Si-H group.

GCMS

The degradation products contained in the "cold ring" fraction were separated by programmed gas chromatography (Fig. 5.8). The m/e values for the parent ions of these products are recorded in Table 5.1, together with their proposed structures. Results from the infrared analysis were considered in making these proposals.

The structures proposed for peaks 2 and 5 are written with the hydrogen substituents attached to different silicon atoms. By interchanging a hydrogen atom with a phenyl group, alternative structures containing both di-hydrogen and diphenyl substituted silicon atoms could be obtained. In this way the structure for peak 5, for example, could be

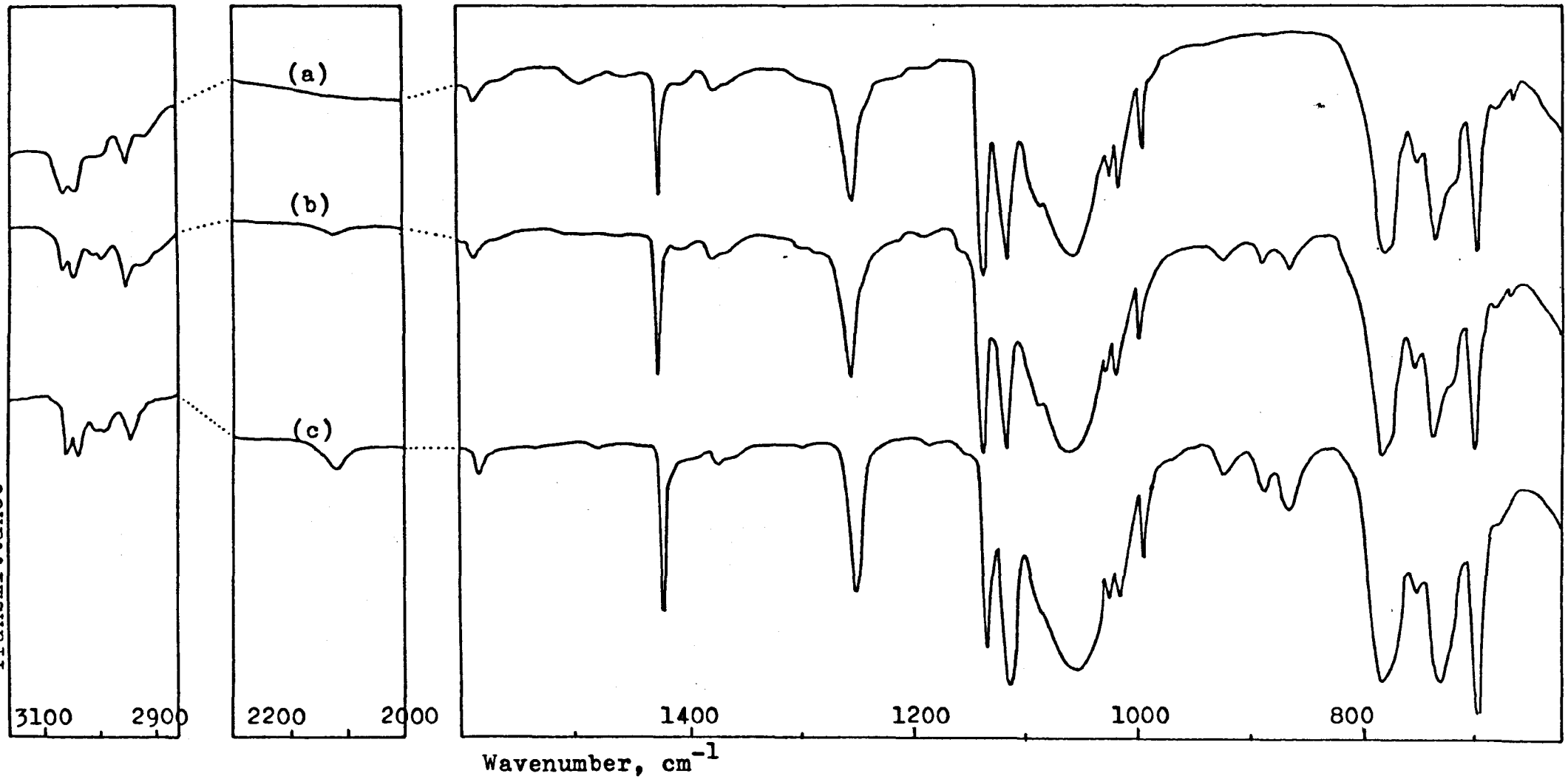


Fig. 5.7 Infrared spectra of the 'cold ring' fractions from MPPS heated isothermally at: (a) 400°; (b) 450°; (c) 500°.

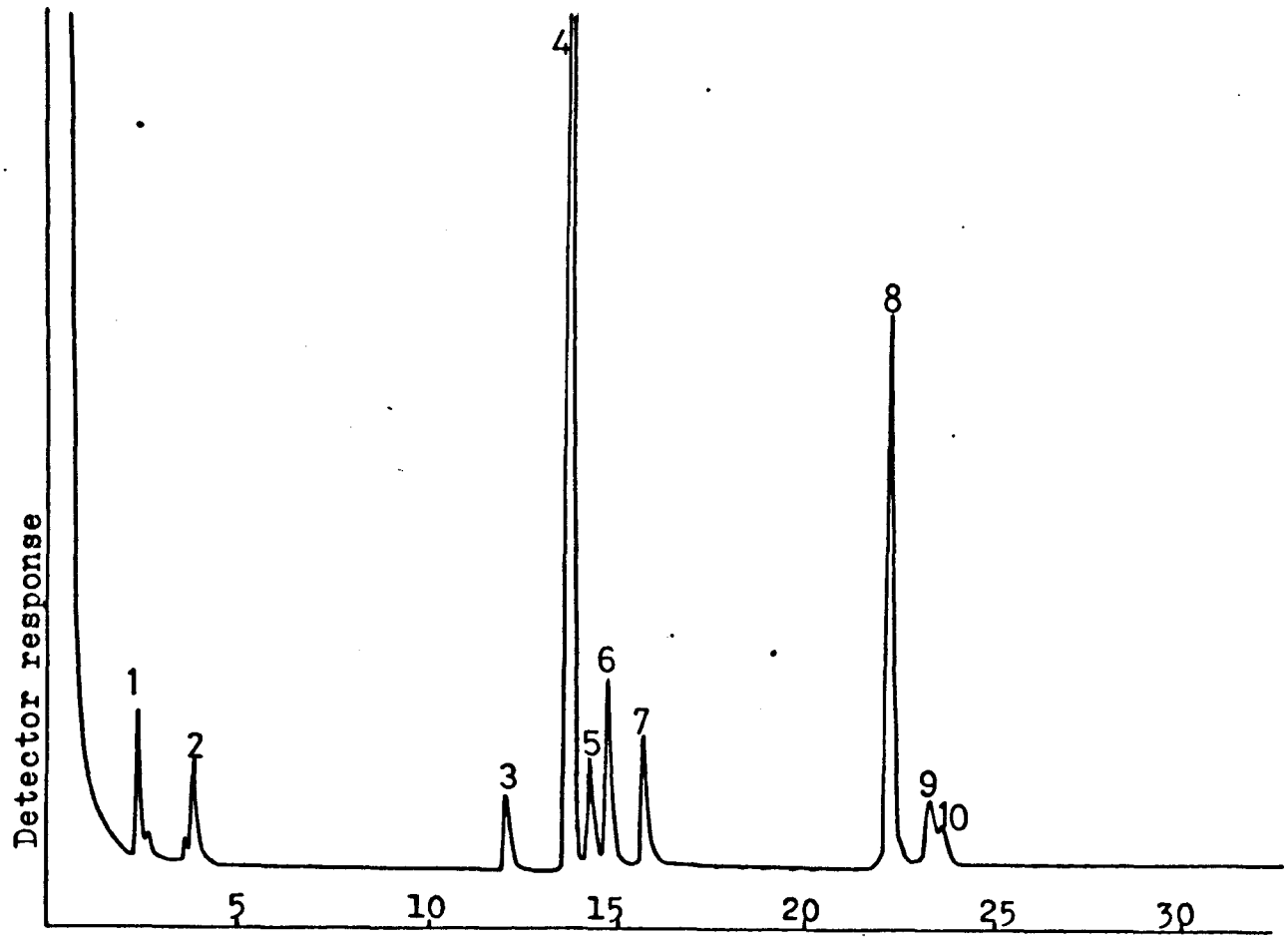


Fig. 5.8 GC trace of the products of degradation of MPPS (1h at 500°). Programme, 5° min^{-1} from 100° to 270°, thereafter held at 270°.

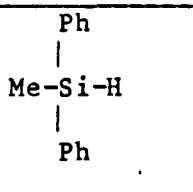
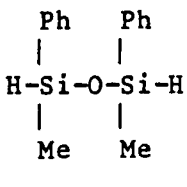
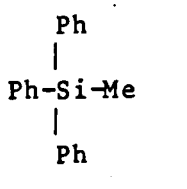
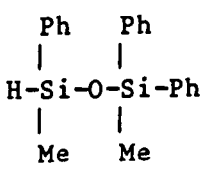
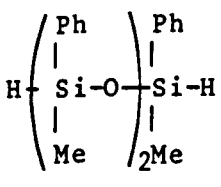
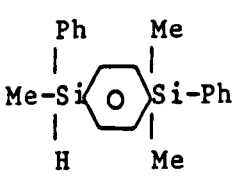
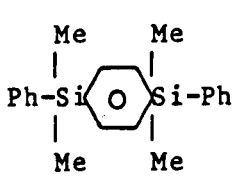
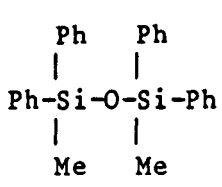
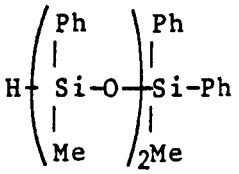
Peak	m/e of parent ion	Proposed structure
1	198	
2	258	
3	274	
4	334	
5	394	
6	332	
7	331(M-15)	
8	410	

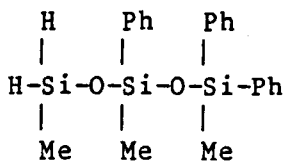
TABLE 5.1

TABLE 5.1 (contd.)

Peak	m/e parent ion	Proposed structure
9	470	
10	No MS obtained	?

GCMS analysis of a mixture of degradation products from MPPS.

written:



The possibility of the formation of these isomers will be discussed later.

3. Residue

Infrared analysis

No changes were apparent in the infrared spectrum of the residue from isothermal heating below 450° when compared with the original polymer. Above 450° the Si-H group reveals its presence by the appearance of absorption bands at 2120 and 920 cm^{-1}. Band broadening also results at the higher temperatures but the wavelengths and relative intensities are unaltered (Fig. 5.9).

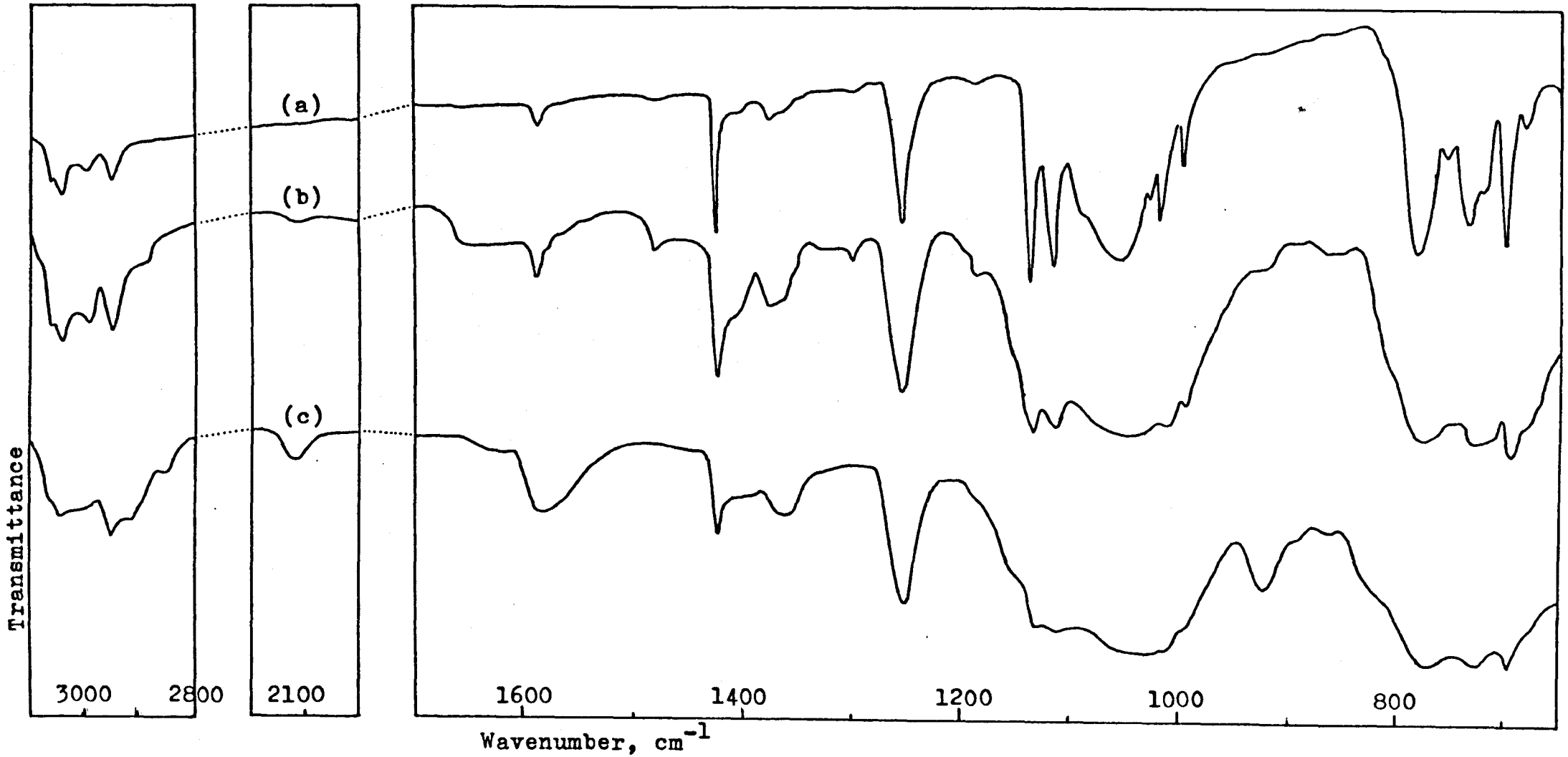


Fig. 5.9 Infrared spectra of the residue from MPPS heated at: (a) 350°; (b) 450°; (c) 500°.

Sol-gel analysis

Insolubility develops in the polymer residue on heating at 400°. However, unlike TMPS, no gel formation was detected at 350°. The soluble fraction, S, was measured and $S + \sqrt{S}$ was plotted against 1/t, the reciprocal of the heating time interval (Fig. 5.10). The graph was essentially linear as predicted by the Charlesby Pinner equation,

$$S + \sqrt{S} = p_o/q_o + \frac{1}{q_o u t}$$

where p_o and $q_o/2$ are respectively the rates of chain scission and crosslinking per monomeric unit and u is the number average chain length. Values calculated for p_o and $q_o/2$ are recorded in Table 5.2 together with the corresponding results for TMPS.

Polymer	Scissions monomeric unit.hour	Crosslinks monomeric unit.hour
TMPS	$1.416.10^{-3}$	$1.723.10^{-3}$
MPPS	$1.819.10^{-2}$	$8.034.10^{-3}$

TABLE 5.2

The uncertainty in the absolute values of the calculated rate constants was discussed previously (Chapter 4.3). However, a relative comparison shows the rate of crosslinking increases when phenyl groups replace methyl groups.

Weight loss measurements

The relationship between the weight loss of MPPS and

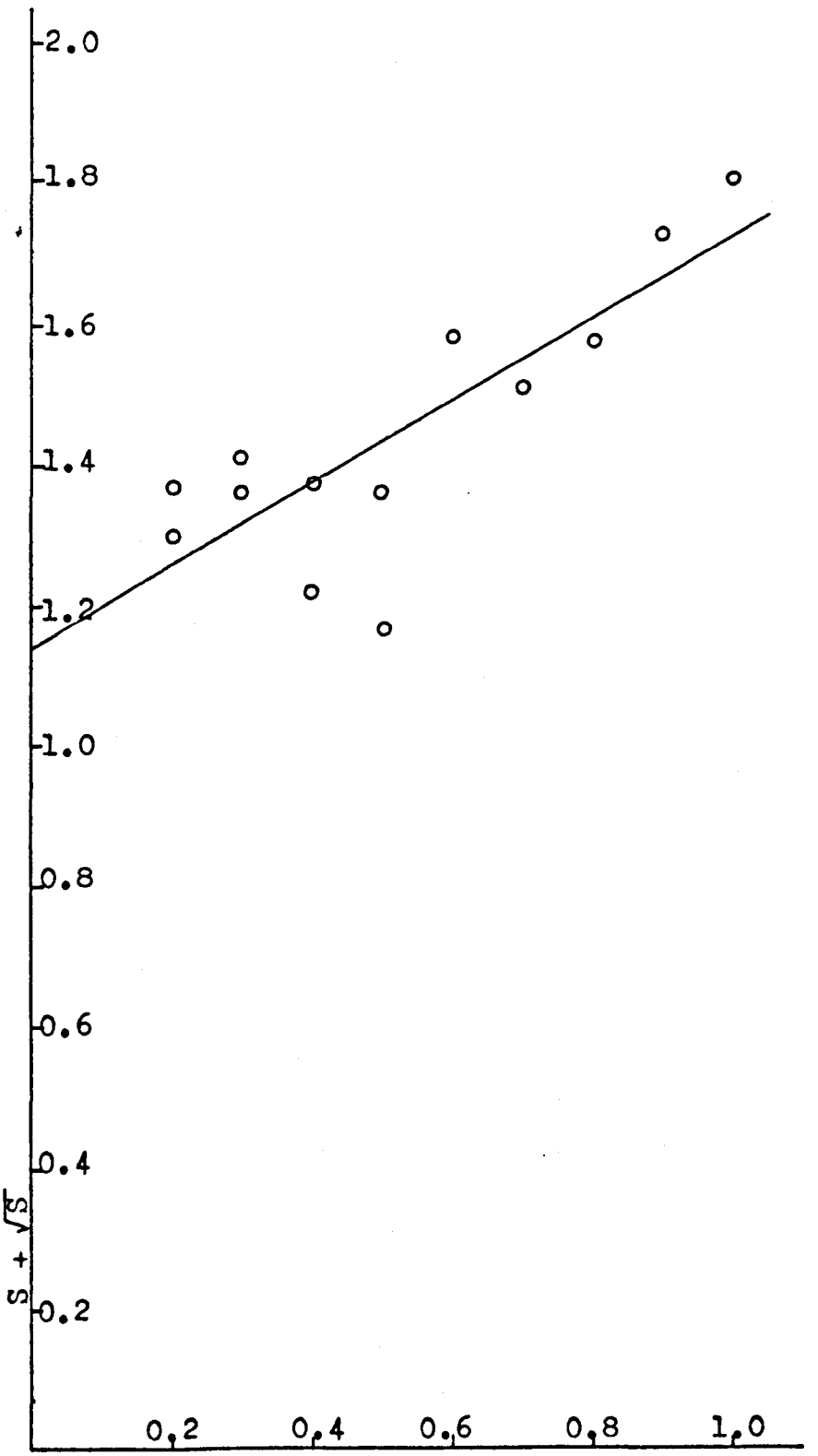


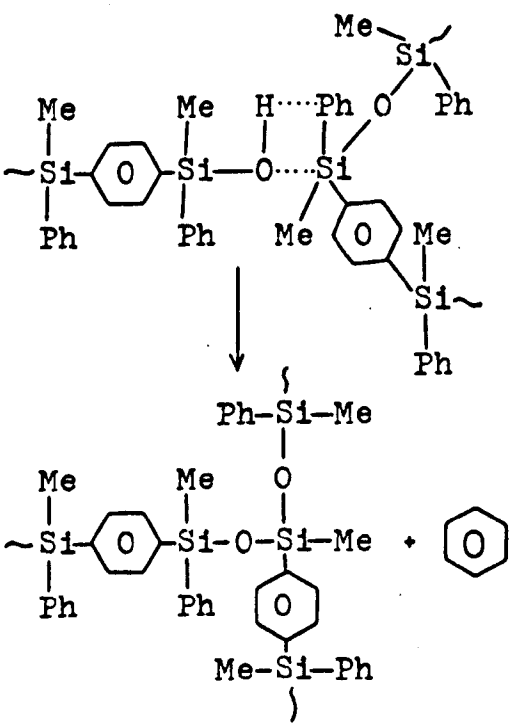
Fig. 5.10 Plot of $S + \sqrt{S}$ against $1/t$ after prolonged heating at 400^{o} of MPPS.

the time of heating at 400° (Fig. 5.11) reveals that the decrease in the residual weight is linear with the heating time interval. Using the method of least squares analysis, the rate of weight loss was calculated as 2.15g/100g/h which is lower than the value of 4.96g/100g/h obtained when TMPS is degraded at 400°.

5.4. Discussion

Many features observed in the thermal degradation of MPPS resemble points previously witnessed in similar investigations of TMPS (Chapter 4) and poly(methylphenylsiloxane) (Ref 10). This is hardly surprising since the structure of MPPS may be regarded as intermediate between the structures of these polymers. Thus it would not seem unreasonable to discuss the breakdown pattern of MPPS in terms of the reactions encountered in the degradation of TMPS and poly(methylphenylsiloxane) (Ref 10).

The appearance of benzene at 370° coinciding with the onset of gel formation is consistent with the theory that the hydroxyl terminals assist cleavage of the Si-Ph bond (Ref 10):



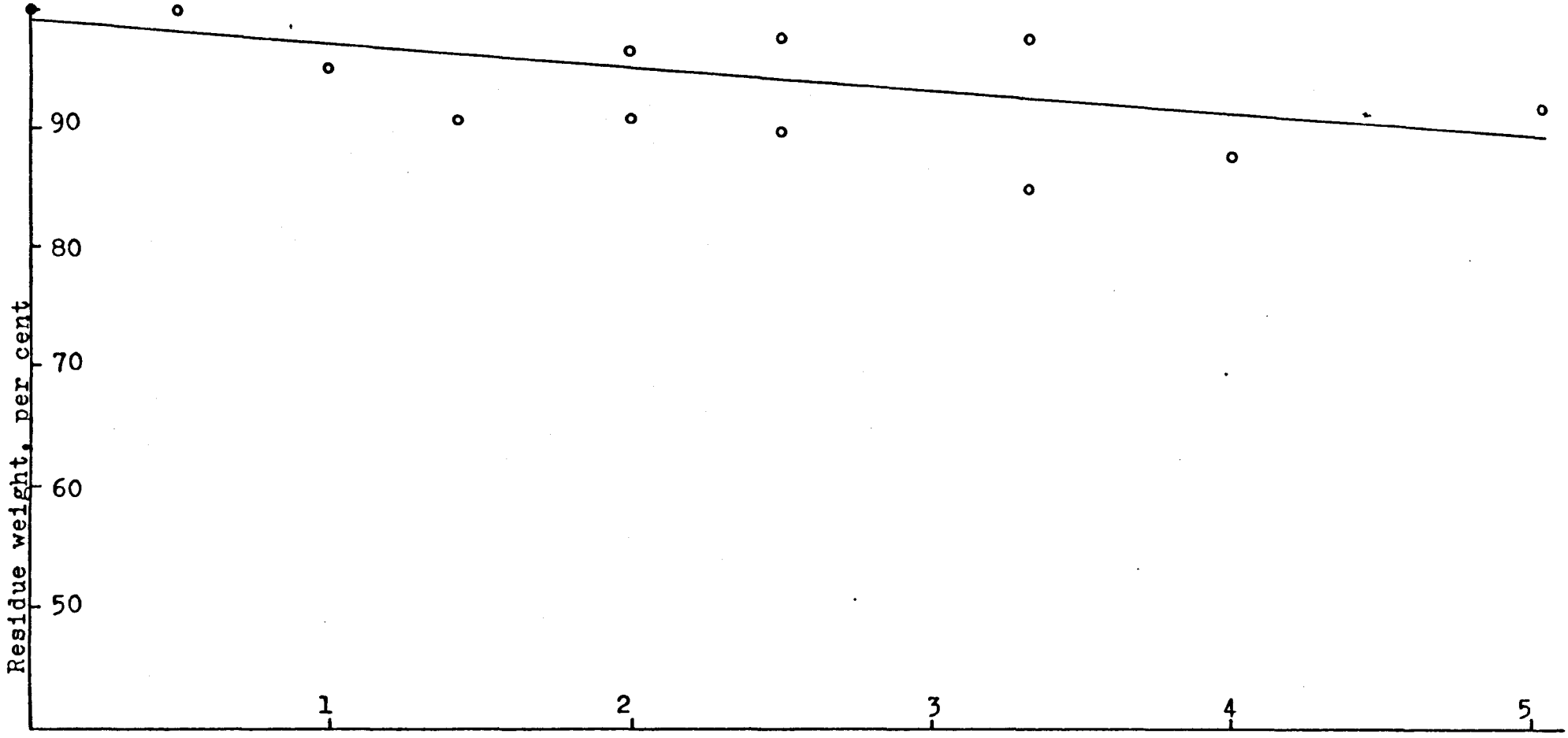
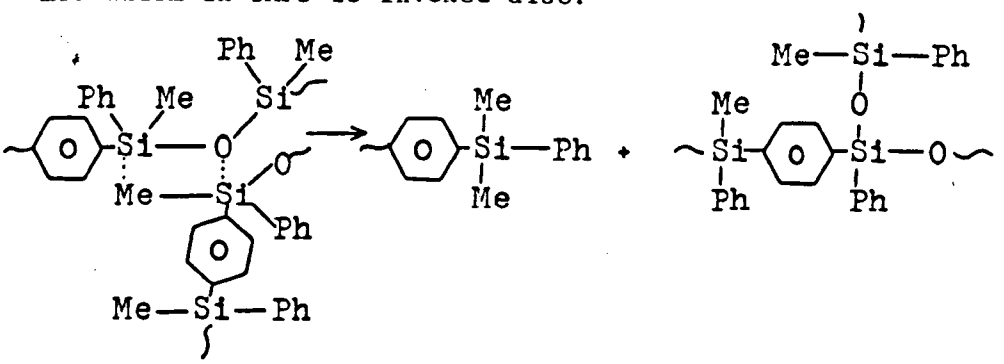
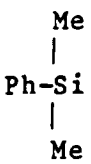


Fig. 5.11 Weight loss of MPPS with prolonged heating at 400°.

A second process, analogous to the chain branching mechanism in TMPS is invoked also:



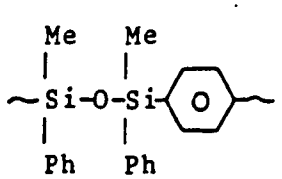
Evidence for this mechanism comes from the presence of



end grouped species in the "cold ring" fraction.

The rates of chain scission and crosslinking, calculated from sol-gel analysis, are greater for MPPS than for TMPS. This may be due, in part, to the electronic effect of the phenyl group. When it is attached to silicon, the phenyl group becomes electron donating and so increases the electron availability at oxygen which in turn facilitates the nucleophilic attack by oxygen at silicon present in both the above mechanisms. It is suggested also that the existance of two chain branching reaction mechanisms in MPPS compared with one in TMPS will contribute to the observed increase in rate.

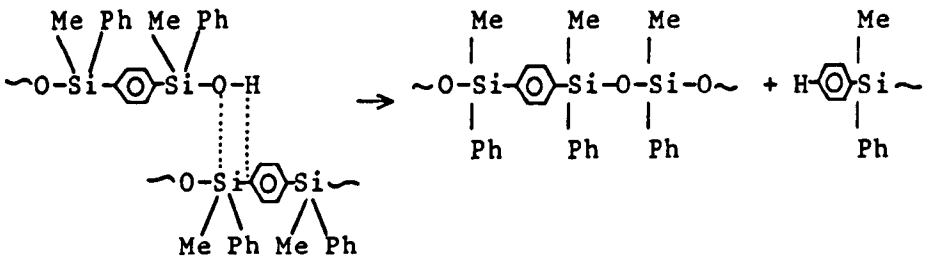
The MPPS backbone is composed of alternating silphenylene and siloxane units:



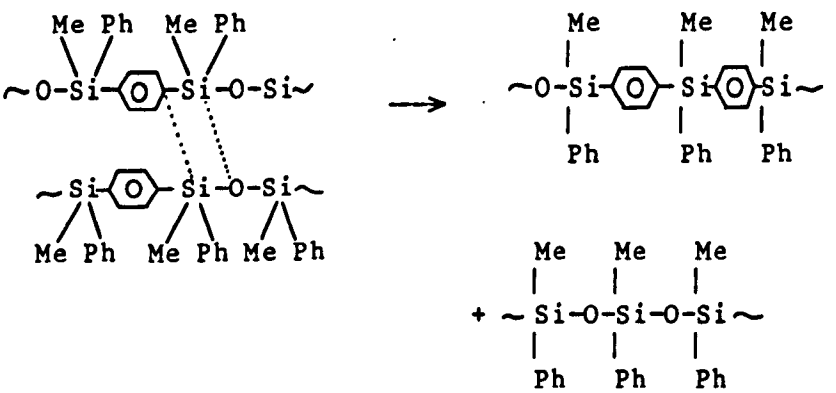
However, several of the degradation products, identified in

Table 5.1, possess structures which indicate that the polydispersity is altered. Two rearrangements are suggested to account for this fact.

The former of the chain branching mechanisms, suggested earlier, involved the reaction between the terminal hydroxyl groups and the bond between silicon and the phenyl substituent. If instead, the hydroxyl group reacted with the silphenylene bond, the nature of the end groups would be altered and adjacent siloxane linkages would be introduced.

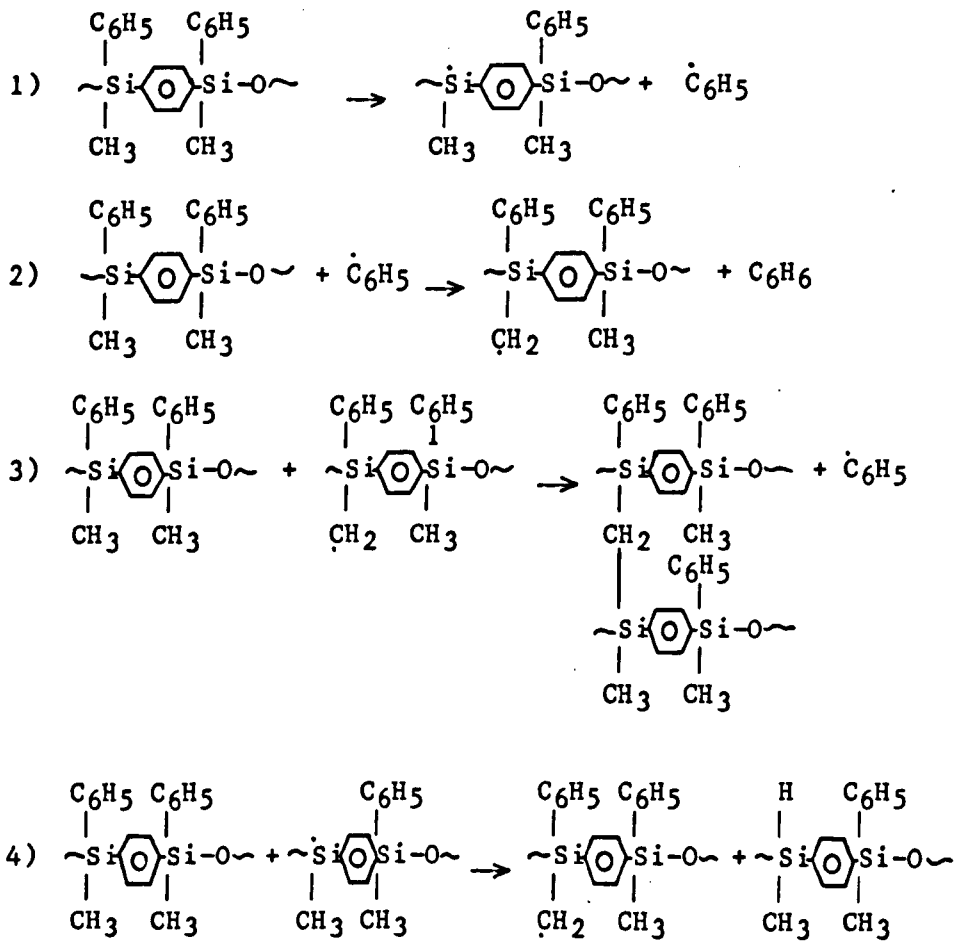


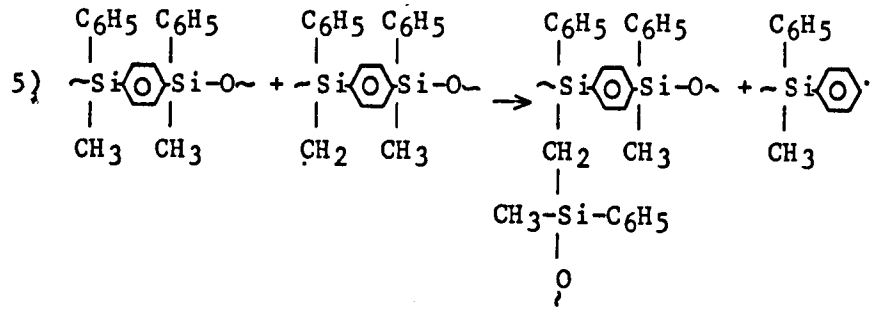
Moreover the rearrangement of siloxane and silphenylene bonds, previously encountered in the formation of the cyclic dimethylsiloxane trimer in the degradation of TMPS, may be invoked:

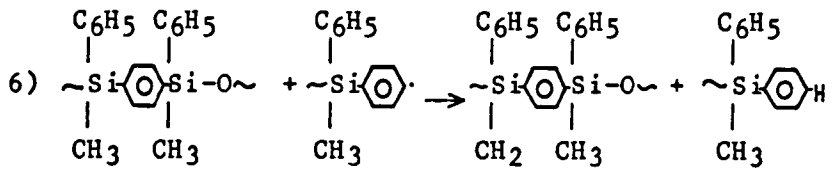


In this case two adjacent silphenylene units and two adjacent siloxane units are formed.

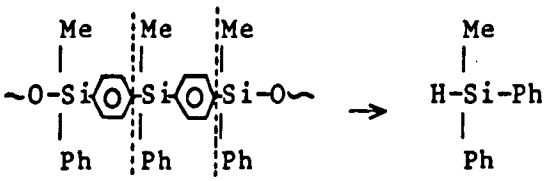
At higher temperatures the production of benzene increases and compounds with Si-H and Si-Ph end groups are formed. The mechanism involving Si-Ph bond scission, proposed originally by Sobolevskii (Ref 16) and present in the thermal breakdown of both TMPS (Chapter 4) and poly(methylphenylsiloxane) (Ref 10), again seems reasonable. This mechanism is apparently more complex for MPPS as scission of the Si-Ph bond may take place either within the polymer backbone or between a phenyl substituent and the polymer backbone. These reactions can be represented in the following general form:



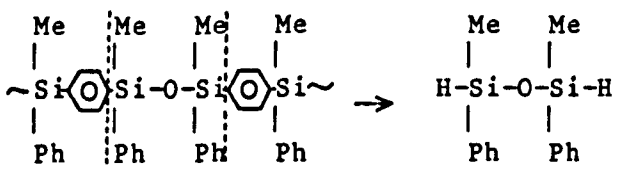




The combined effect of the low temperature rearrangement with bond scission at higher temperature accounts for all the products listed in Table 5.1. The formation of methyldiphenylsilane, for example, requires rearrangement of the polymer chain prior to Si-Ph bond scission.



A product such as the one responsible for peak 2 in the GCMS analysis can result from scission in an unmodified section of the chain.



Thermogravimetry demonstrates that MPPS is thermally more stable to weight loss than TMPS. It is thought that the phenyl substituents act in two ways to increase the stability. From a steric point of view, the increased bulk

of the phenyl group reduces the chain flexibility. Secondly the favourability of the chain branching mechanism increases. Both effects oppose volatile formation and are reflected in the increased threshold temperature and the decreased overall weight loss.

5.5. Summary

The effect of replacing dimethyl-substituted silicon with methylphenyl-substituted silicon is to increase the thermal stability. At the lower degradation temperatures several rearrangement reactions occur causing gel formation, a change in the polydispersity and benzene production. When the temperature is raised the mechanism changes to one of Si-phenyl or Si-phenylene bond scission. Benzene production increases and a mixture of short chain oligomers containing Si-H or Si-Ph groups are formed. An appreciable quantity of insoluble residue remains.

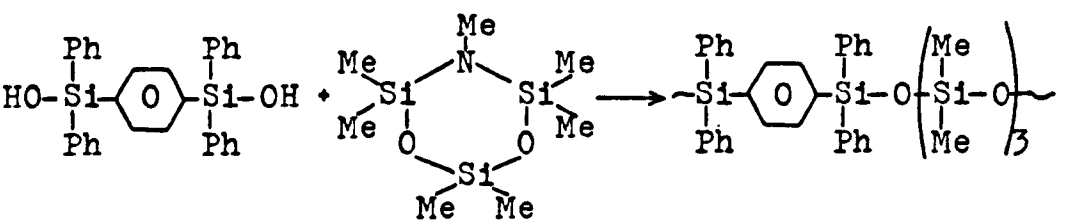
CHAPTER 6

POLY(TETRAPHENYL-p-SILPHENYLENE-SILOXANE)

6.1. Introduction

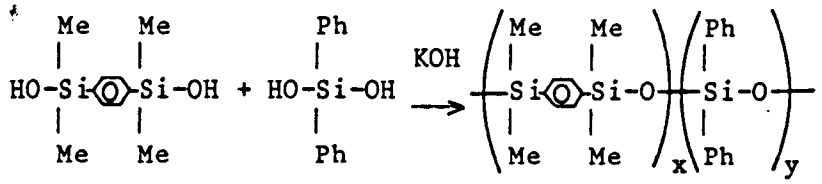
Comparative studies of the thermal stabilities of MPPS and TMPS reveal that the methylphenyl substituted silphenylene-siloxane is more resistant to heat than the dimethyl substituted polymer. Continuing further along this sequence of materials the thermal stability of poly(tetraphenyl-p-silphenylene-siloxane), TPPS, will be investigated.

The preparation of several silphenylene-siloxane polymers having extended siloxane segments between the silphenylene units and containing diphenyl substituted silicon atoms have been reported (Ref 18). Breed and his co-workers (Ref 23) attempted a polymerization between p-phenylenebis(diphenylsilanol) and a cyclic dimethylsiloxazane.



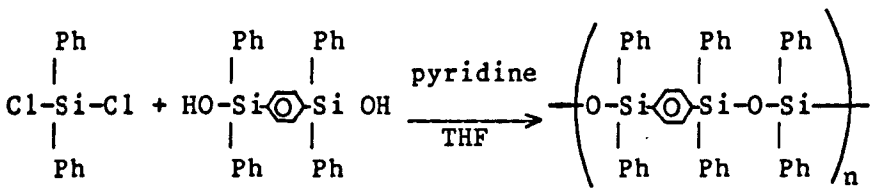
Difficulties were encountered in this reaction as prolonged heating rendered the polymer insoluble. A condensation reaction between p-phenylenebis(dimethylsilanol) and

diphenyldihydroxysilane, aided by the presence of the alkaline catalyst, KOH, met with more success (Ref 25).



No information was given on the thermal stabilities of these polymers.

A polymer containing diphenyl substituted silicon atoms only was prepared by Wu (Ref 50).



n = 3-50

At high temperatures the weight loss of such a polymer, where n= 12, was reported to be less than for DMS having similar molecular weight. Heating the polymer to 500° caused embrittlement although no changes were observed in the DTA.

No mention in the literature of the alternating silphenylene-siloxane polymer containing only diphenyl substituted silicon could be found. Attempts to prepare this polymer from p-phenylenebis(diphenylsilane) are described in Chapter 3. The absence of absorptions in the infrared or resonance signals in the proton n.m.r. spectra (Fig 3.8,3.9) due to the Si-OH group indicate that some condensation has occurred. However, the failure to obtain accurate results from membrane osmometry suggests that the molecular weight is low. Bearing this in mind, a brief look at the thermal

stability of TPPS was undertaken.

6.2 Thermal Analysis

The technique adopted in the investigation of the thermal decomposition of MPPS to detect the formation of volatile material was employed again. A slight rise in the TVA trace from the base line at temperatures above 313° is observed (Fig. 6.1). Results from the ultraviolet and infrared spectra of the gaseous products identified benzene as the sole component in this fraction (Fig. 6.2 and 6.3). Prolonged heating of the polymer at 500° resulted in 100% weight loss which, apart from a small quantity of benzene, could all be accounted for as "cold ring" fraction.

The infrared spectrum of the "cold ring" fraction collected after heating TPPS at 390° for 1 hour is virtually indistinguishable from that of the original polymer (Fig. 6.4). Degrading at higher temperatures up to 500° does not alter the nature of the products formed.

TG demonstrates that the weight loss occurs in two stages (Fig. 6.5). The threshold weight loss temperature is 210°, which is about 100° lower than the onset of the formation of benzene. Two broad endotherms are present in the DSC trace (Fig. 6.6) at temperatures corresponding to the two components of the weight loss curve. The sharp endotherms at 130° and 150° are attributed to the melting behaviour of the polymer. The melting temperature observed in the DSC trace is considerably lower than the value quoted in the literature for the melting point of p-phenylenebis(diphenylsilanol) (224-6°; Ref 31). This provides another indication that

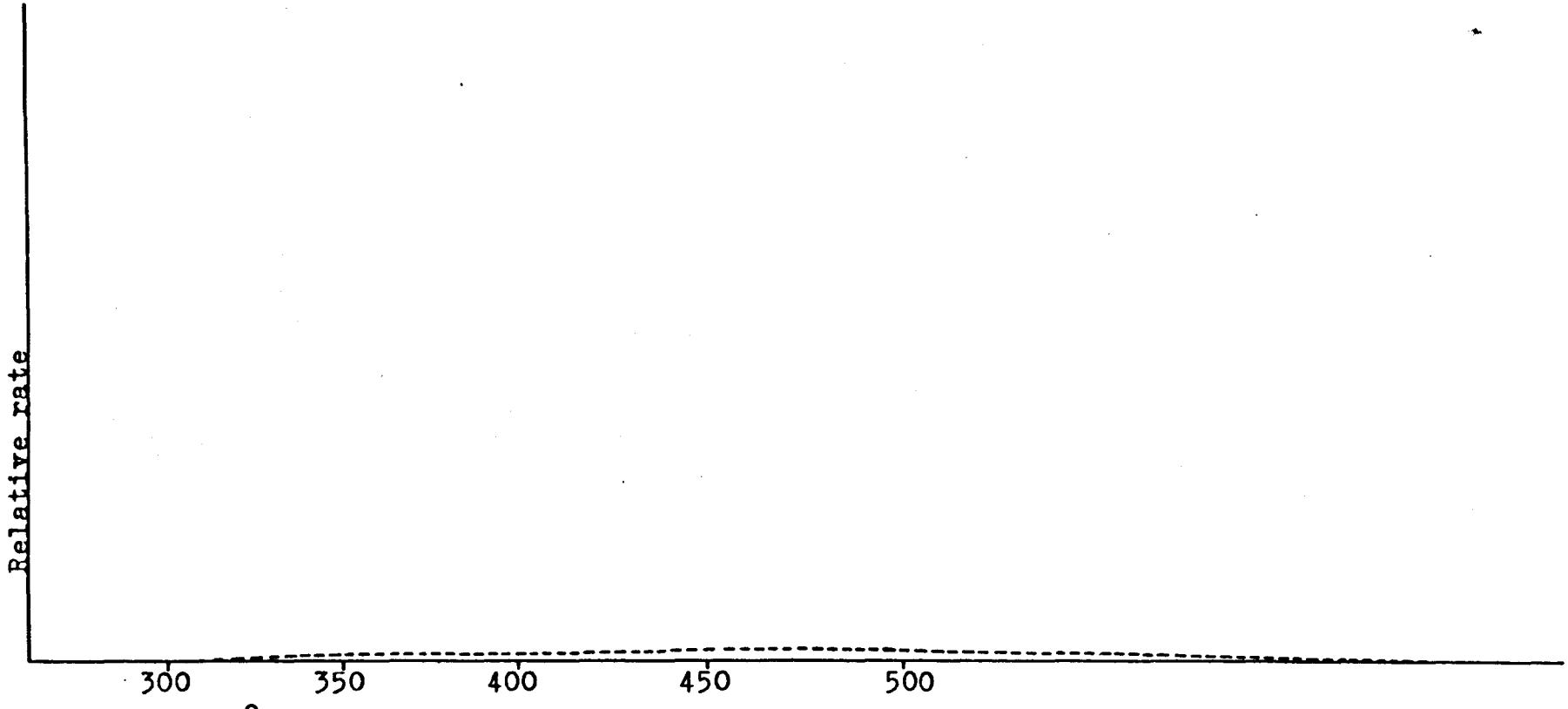


Fig. 6.1 TVA trace for TPPS. Heating rate at 10^{o} min^{-1} from ambient to 500^{o} and thereafter maintained at 500^{o}.

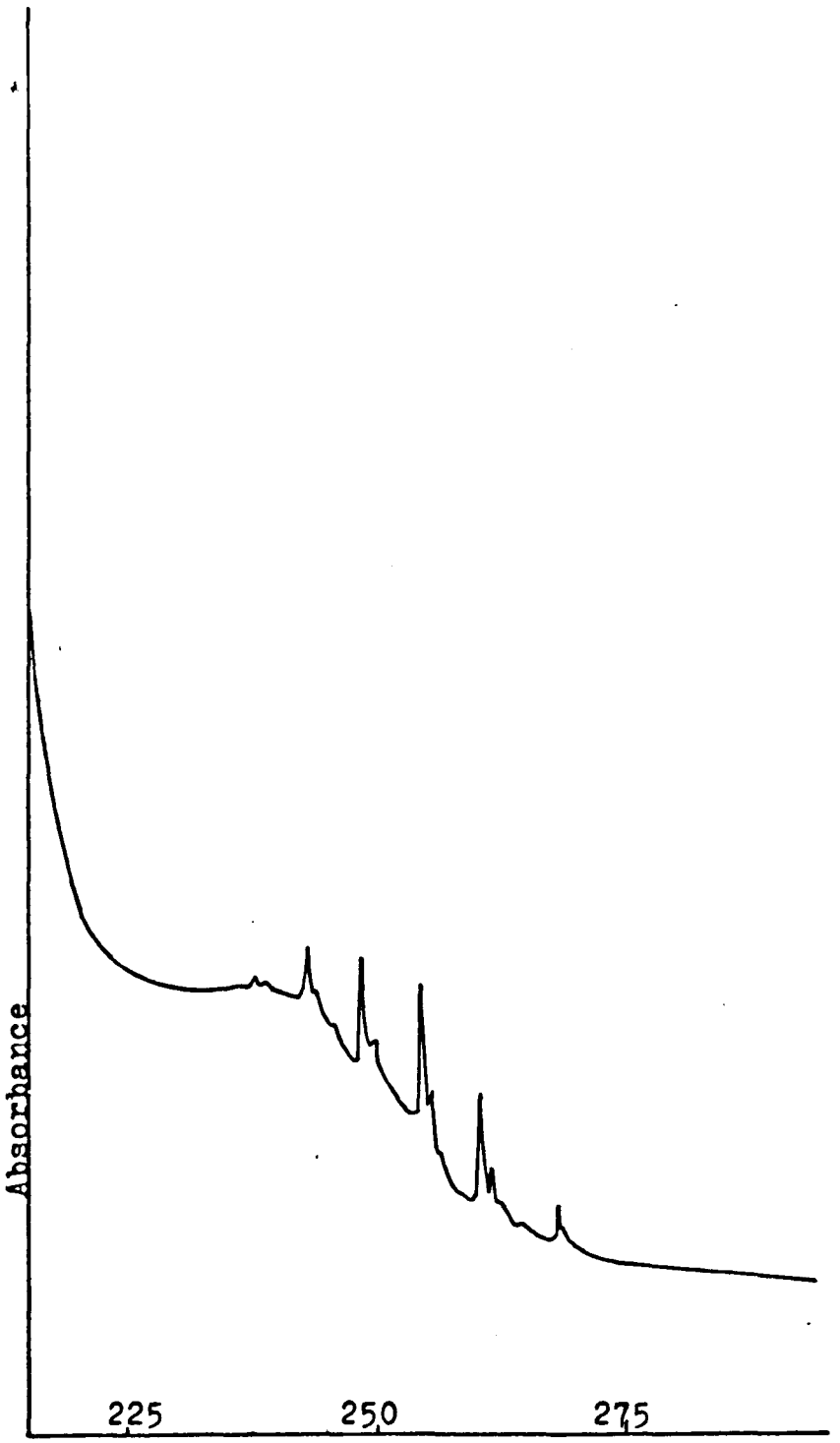


Fig. 6.2 Ultraviolet spectrum of the gaseous products of degradation from TPPS heated to 500°.

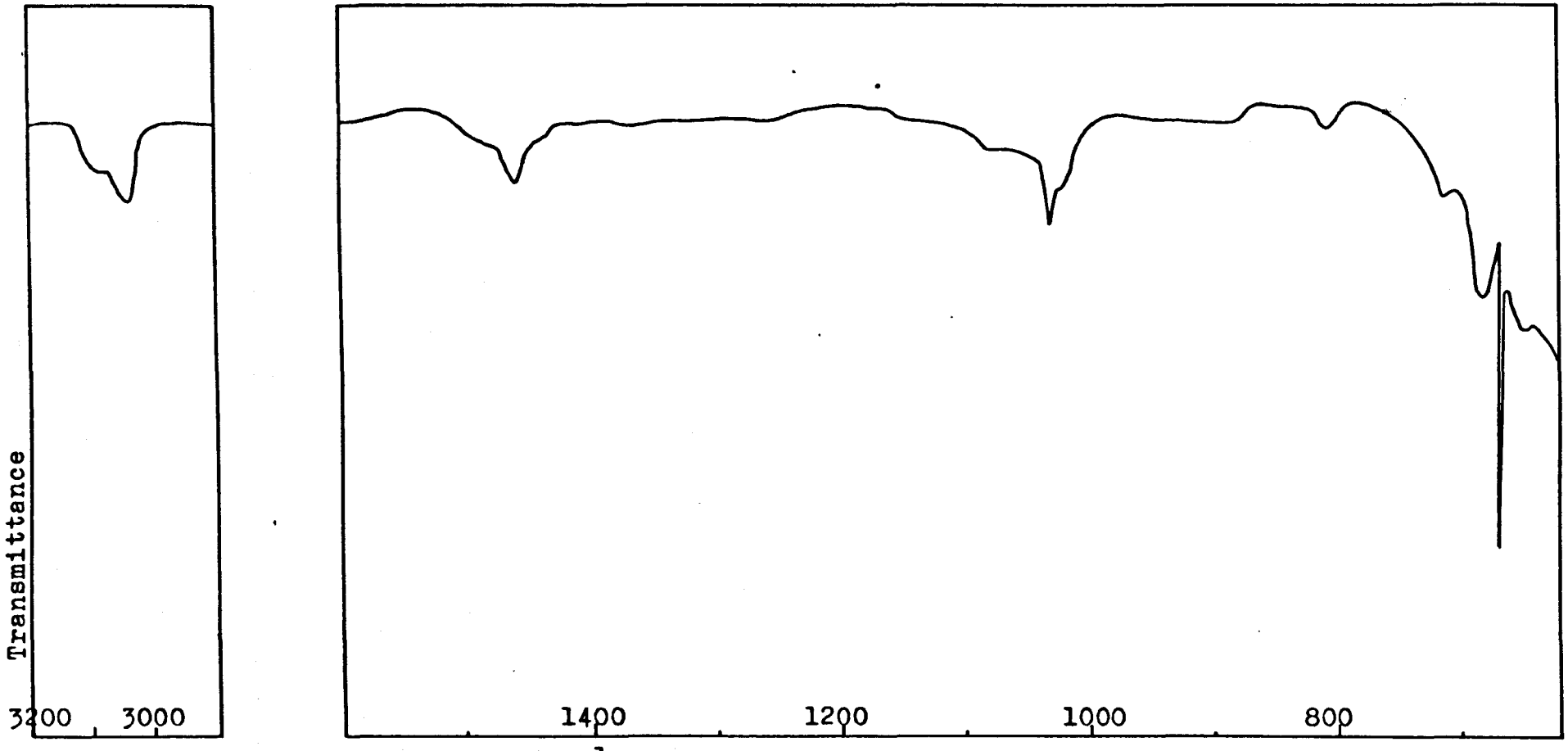


Fig. 6.3 Infrared spectra of the gaseous products of degradation from TPPS heated to 500°.

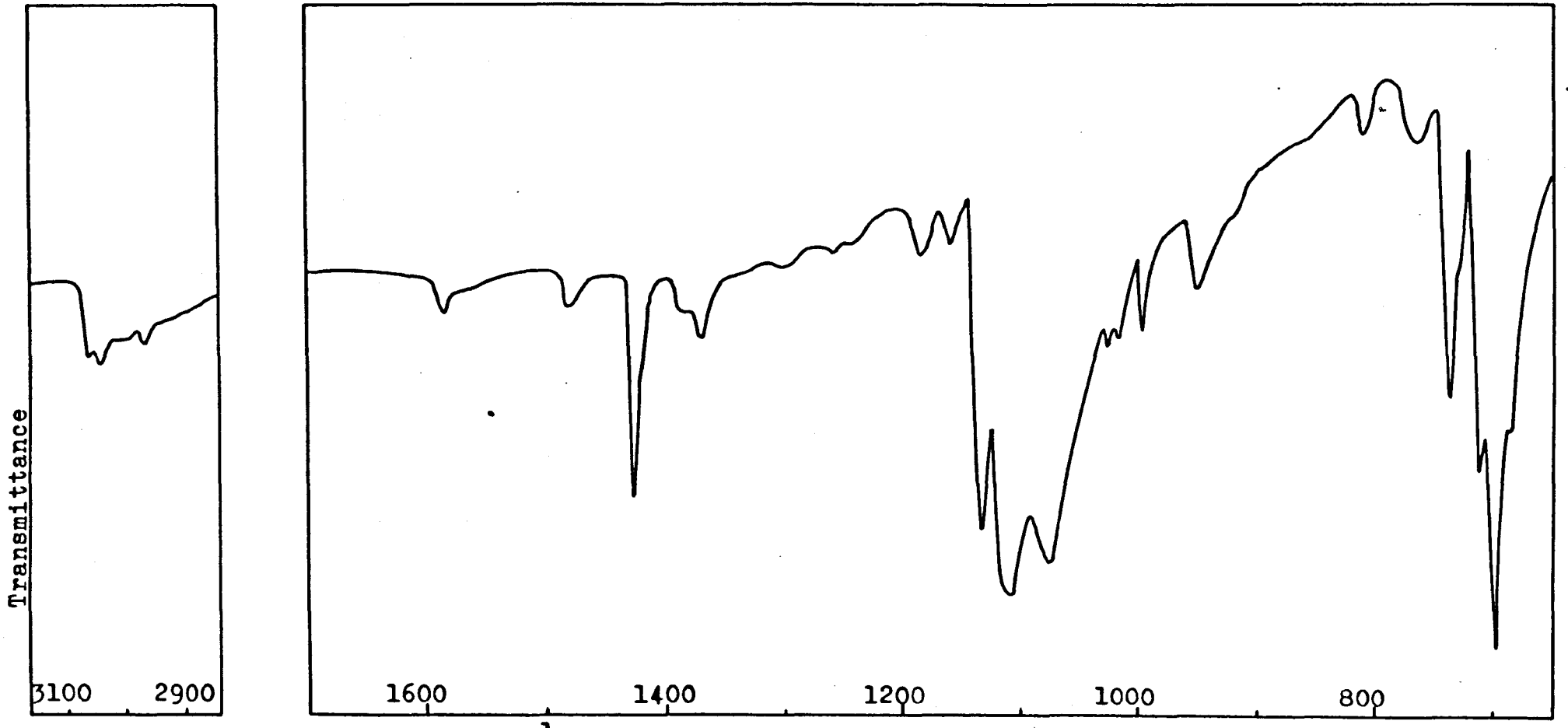


Fig. 6.4 Infrared spectrum of the 'cold ring' fraction from TPPS heated to 500°.

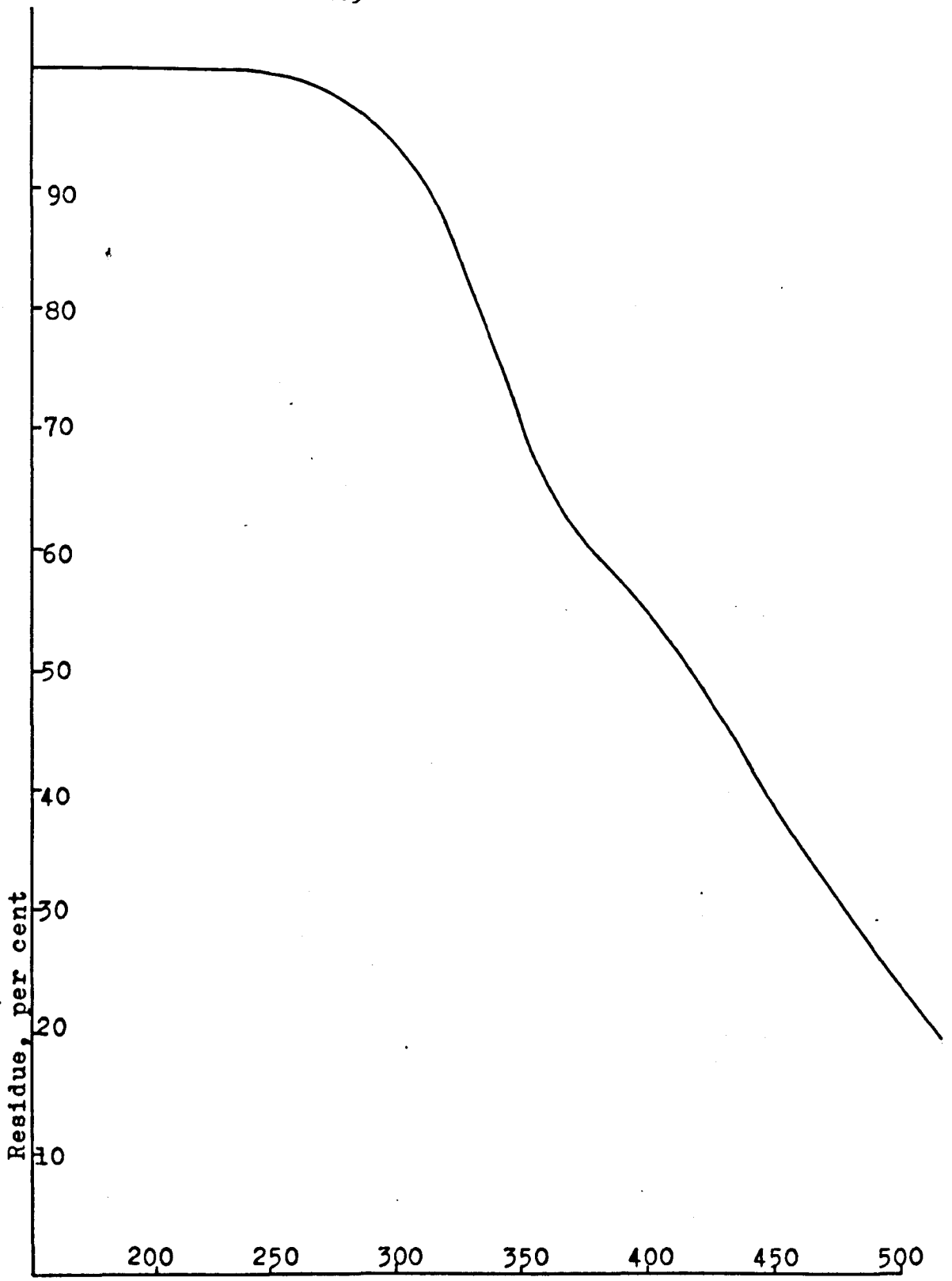


Fig. 6.5 TG trace for TPPS.

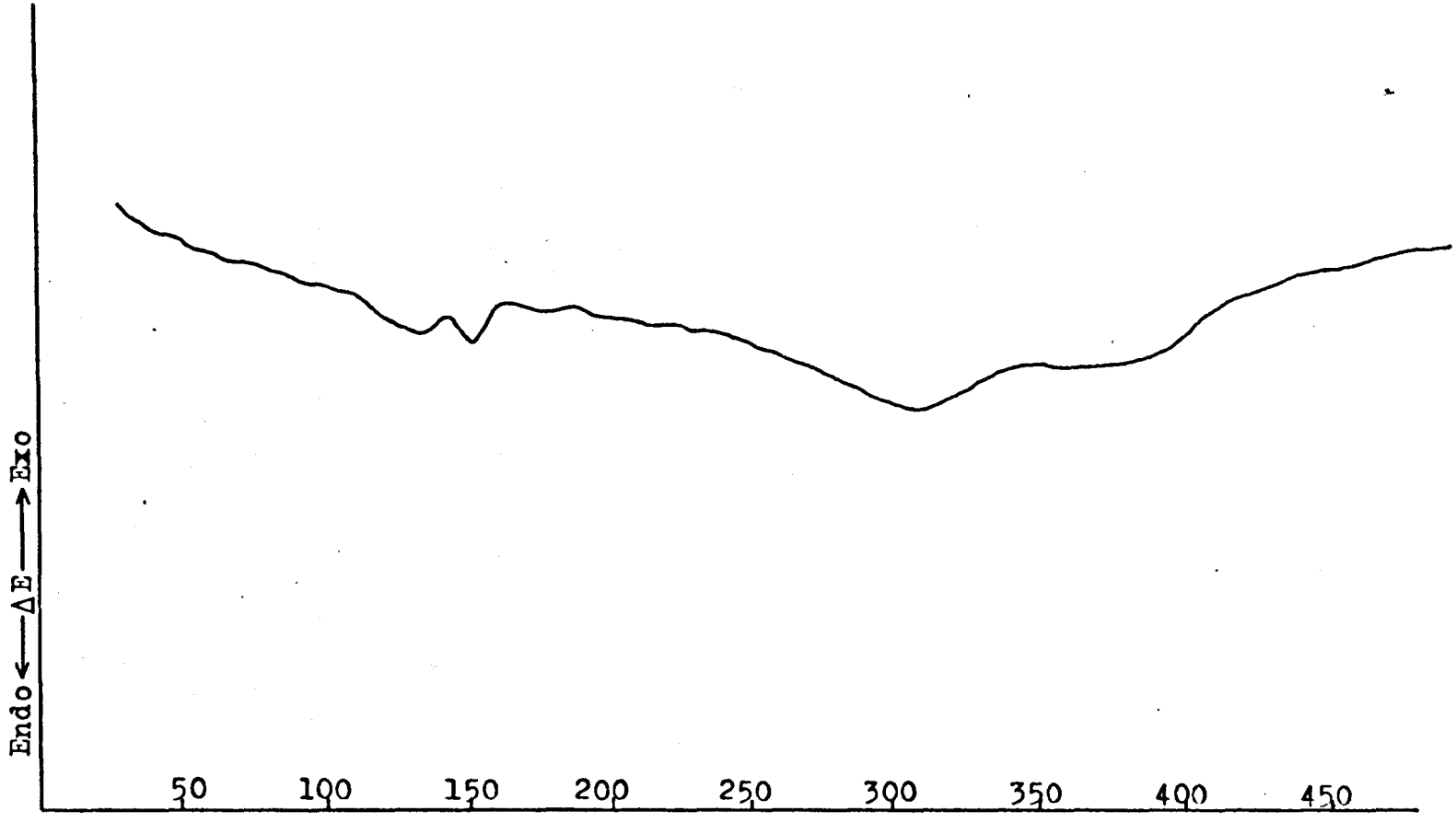


Fig. 6.6 DSC trace for TPPS.

polymerization has occurred to some extent.

6.3. Discussion

Two of the experimental observations might lead to the assumption that, owing to its low molecular weight, the polymer has volatolised without undergoing a chemical change. The observations in question were:

(a) the close resemblance of the infrared spectra of the original polymer and the "cold ring" fraction,

(b) the independence of the nature of the "cold ring" fraction on the temperature of degradation.

The formation of benzene, however, disproves this unlikely explanation. It is suggested that the products are low molecular weight oligomers, similar in structure to the parent polymer molecule. Since these are formed at the lower temperatures of degradation, the reaction mechanism may be regarded as one of rearrangement.

TG analysis demonstrates that TPPS is thermally less stable to weight loss than DMS. The low molecular weight of the polymer may be responsible for this decreased stability. Alternatively the steric effect of having two large phenyl groups attached to each silicon atom may favour the degradation reaction. It is suggested that these two factors are interrelated. That is the molecular weight is low due to the reluctance of the diphenyl substituted monomer to polymerise.

These results are not unexpected if they are compared with observations concerning diphenyl substituted siloxane

polymers. Andrianov et al investigated the polymerization of dimethylmethylphenyl and dimethyldiphenyl cyclosiloxanes in the presence of acidic or basic catalysts. Both the molecular weight (Ref 51) and the rate of polymerization (Ref 52) decrease significantly as the phenyl content of the monomer mixture is increased. More recently Macfarlane (Ref 39), after making several attempts to prepare poly(diphenylsiloxane), concluded that high molecular weight polymer is not readily prepared.

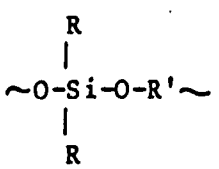
It is thus concluded that high molecular weight TPPS cannot be prepared in a manner analogous to TMPS or MPPS. In view of the failure to obtain the high molecular weight polymer, the degradation behaviour of TPPS was not investigated further.

CHAPTER 7

THE SYNTHESIS AND THERMAL STABILITY OF TWO ARYLOXYSILANE POLYMERS

7.1. Introduction

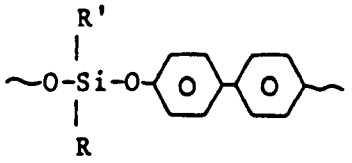
Perhaps one of the most outstanding features of the polysiloxanes is their ability to maintain useful properties at high temperatures. For this reason much interest has centred on polymers with modified siloxane structures in the search for new materials with improved mechanical strength combined with a good resistance to heat. One such modification is the insertion of aromatic groups into the backbone of the siloxane polymer. The polyaryloxysilanes, which may be represented by the general formula:



where R' is an aromatic unit and R may be either aromatic or aliphatic, are thus of considerable interest.

Arsen'eva and his co-workers (Ref 53), in an investigation of the hydrolytic and thermal stability of some polyaryloxysilanes found that both are dependent on the nature of the aromatic unit and the substituents attached to the silicon atom. It was concluded that the stability of the aryloxysilane polymer containing diphenyl substituted silicon atoms exceeded that of either the methylphenyl or dimethyl substituted polymers. A comparison of the thermal

stabilities by Dunnavant et al (Ref 54) of polymers with the general structure:



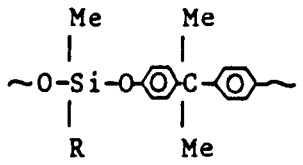
R = Me or Ph

R' = Me or Ph

using TG supported the claim by Arsen'eva. It was also noted that the methylphenyl substituted polymer was thermally more stable to weight loss than the dimethyl substituted material.

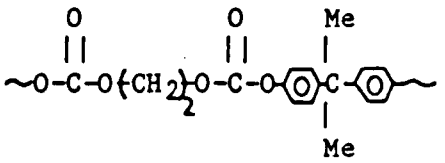
Curry and Byrd (Ref 55) prepared a series of polyaryloxysilanes from several organic diols, including one aliphatic diol. The substituents on the silicon atom were in all cases the phenyl group. Thermogravimetry demonstrated that the thermal stability is markedly lower for polyaryloxysilanes synthesised from aliphatic diols than from aromatic diols. However considerable variation was observed in the stabilities of the polymers originating from the different types of aromatic diol.

In a more recent paper (Ref 56) the thermal stabilities of several copolymers, where one of the comonomers was bisphenol-A, were compared with the aid of TG. These included copolymers of bisphenol-A with the monomer units of poly(dimethylsiloxane) or poly(methylphenylsiloxane)to give polymers with the following structure:



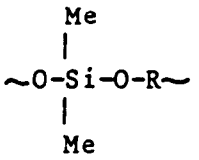
R = Me or Ph

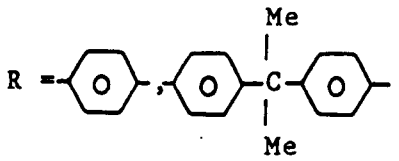
The second group of polymers consisted of polycarbonates from bisphenol-A and various glycols such as ethylene glycol:



The siloxane related copolymers were found to be relatively more stable to weight loss, the methylphenyl substituted polymer exceeding that of the dimethyl substituted material.

The effect of replacing varying amounts of oxygen atoms by arylene groups was considered in the preceding chapters where the thermal stabilities of several silphenylene-siloxane polymers were discussed. This chapter is concerned with those siloxane polymers where the arylene units replace alternate silicon atoms. More specifically, the thermal degradation behaviour of two aryloxysilane polymers will be considered. The polymers in question were prepared in a condensation polymerization between dimethyldianilinosilane and either bisphenol-A or hydroquinone and may be represented by the general structure:

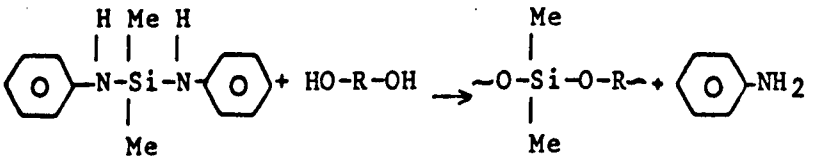


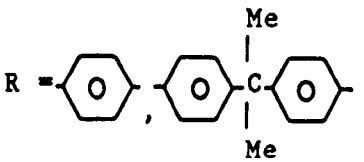


From a brief look at the thermal stabilities of these polyaryloxysilanes it is hoped that some indication of the potential value of further research in polymers of this type will emerge.

7.2 Synthesis

The aryloxysilane polymers were obtained in a melt polymerization of dimethyldianilinosilane with either hydroquinone or bisphenol-A.





Preparation of the dianilinosilane monomer involved a condensation reaction between dimethyldichlorosilane and aniline. A large excess of aniline was present.

$$Me_2SiCl_2 + 4C_6H_5NH_2 \rightarrow (C_6H_5NH)_2SiMe_2 + 2C_6H_5NH_2.HCl$$

The organic diols were obtained from commercial sources, but in each case they were recrystallised from ethanol prior to the polymerization.

1. Dimethyldianilinosilane

Freshly distilled aniline (4.8 mole: 437 ml) was placed in a r.b. flask with toluene (400 ml). A mixture of dimethyldichlorosilane (1.0 mole: 121 ml) and toluene (250 ml) was added dropwise to the flask. Constant agitation of the flask contents was maintained throughout both the addition and a subsequent 45 minute period of reflux. After cooling overnight the aniline chloride precipitate was removed by filtration, washed with toluene and discarded. Distillation of the filtrate removed the toluene and the unreacted aniline and left a brown solid. The final product was obtained by recrystallising the solid twice from methylene chloride. This was characterised from its infrared spectrum and melting point of 41-43°.

2. Polyaryloxysilane

Equimolar amounts of dimethyldianilinosilane and the aromatic diol were mixed in the solid state before placing in a three-necked flask equipped with nitrogen inlet, thermometer and liquid take-off condenser. The flask and contents were flushed out thoroughly with dry, "white spot" nitrogen before heating commenced. After an initial rapid rise in temperature to 120°, it was increased further to 320°over a period of 4 hours and thus maintained for 1.5 hours before allowing the flask contents to cool. Throughout this time a steady flow of nitrogen was maintained. The resulting polymer was purified by dissolving in toluene and reprecipitating from methanol.

7.3. Characterisation

1. Infrared spectroscopy

The infrared spectra of the aryloxysilane polymers from hydroquinone and bisphenol-A are illustrated in Figures 7.1 and 7.2 respectively. Assignments for the major absorption bands are given in Table 7.1. Evidence for the formation of the polyaryloxysilanes is provided by the appearance of the band characteristic of the $Si-O-C_{aryl}$ group at 940-910 cm^{-1} and the absence of the N-H absorption band at 3400 and 1175 cm^{-1}.

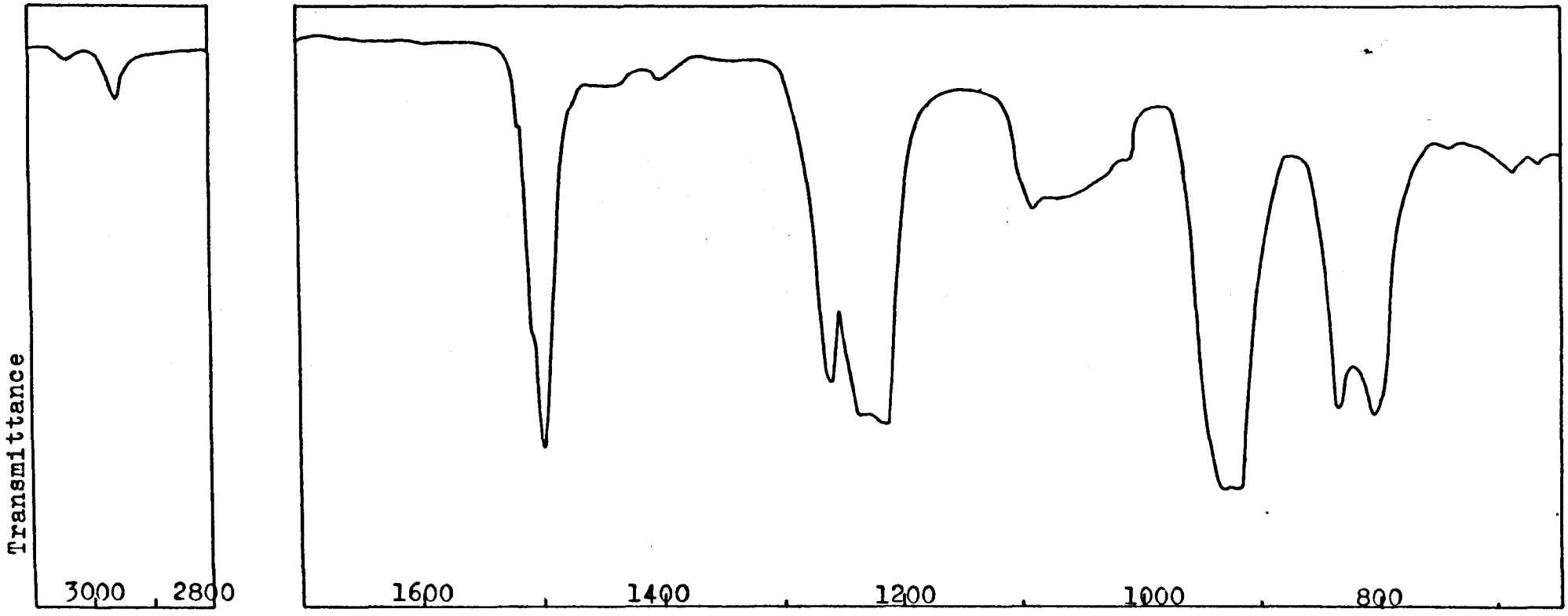


Fig. 7.1 Infrared spectrum of the polyaryloxysilane prepared from hydroquinone.

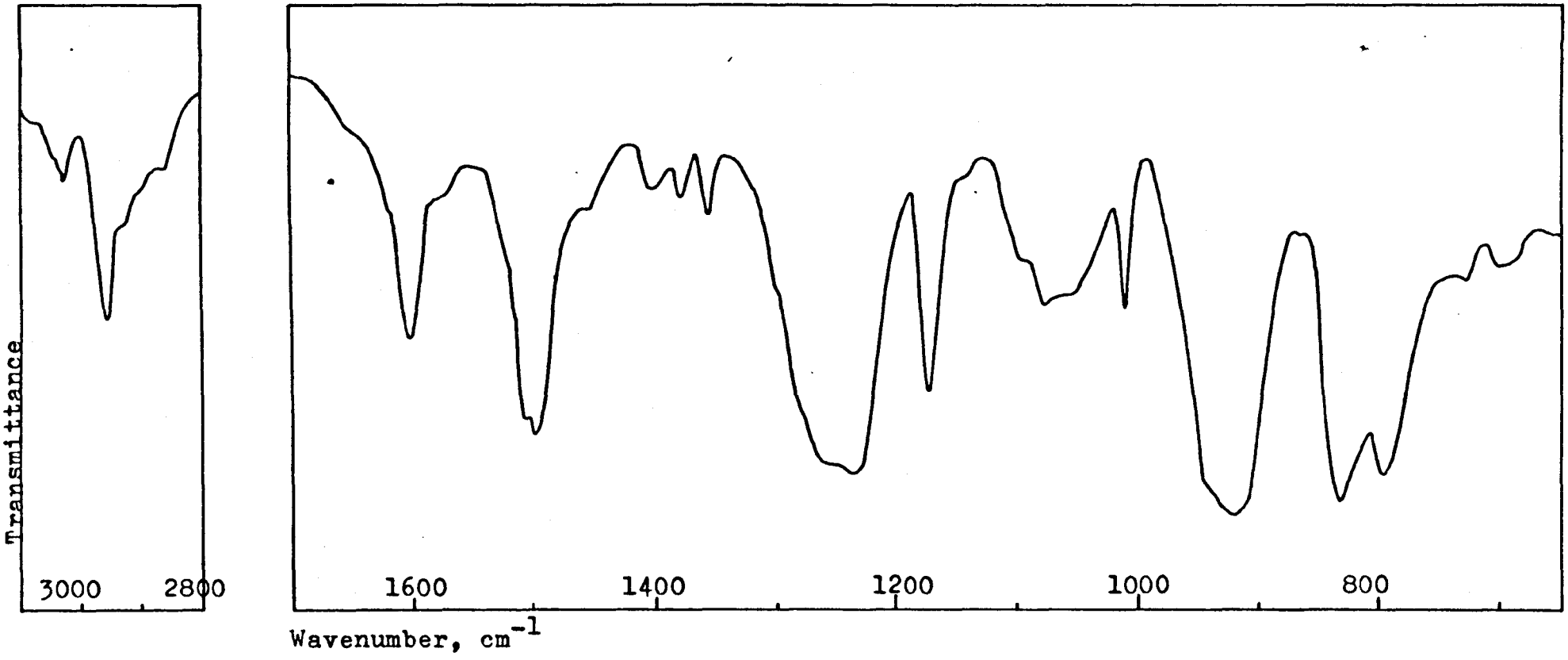


Fig. 7.2 Infrared spectrum of the polyaryloxysilane prepared from bisphenol A.

Group	Band cm^{-1}	Remarks
Aryl C-H	3100-3000	C-H stretching
Alkyl C-H	3000-2860	C-H stretching
Aromatic ring absorptions	1600 and 1495	
Isopropyl radical	1405, 1380 and 1360	
Si-Me	1260	Symmetric CH_3 deformation
Si-O-C	1240-1210	
	1180	Present in spectrum of bisphenol-A
Si-O	1100-1000	
Si-O-C	940-910	Si-O-C stretching mode
1,4-disubstituted benzene ring	840	C-H out of plane deformation
$Si-CH_3$	805	

TABLE 7.1

2. Membrane osmometry

Both polymers were soluble in toluene which enabled the number average molecular weights to be measured using membrane osmometry. The results are recorded in Table 7.2.

Aromatic diol present in polymerization	Mn
Hydroquinone	35100
Bisphenol-A	30500

Table 7.2

7.4. Thermal Analysis

Thermogravimetry was employed to compare the thermal stabilities of the aryloxysilane polymers (Fig 7.3). A threshold weight loss temperature of 275° was common to both polymers with the rate of weight loss being greater for the polyaryloxysilane originating from hydroquinone.

The sharp endotherm in the DSC trace (Fig. 7.4) of the hydroquinone polymer at 77-79° is indicative of the melting temperature of the polymer. A broader endotherm ranging from 310-410° may be due to the degradation reaction. A similar broad endotherm was observed from 330-410° in the DSC trace of the bisphenol-A polymer (Fig. 7.4). However the absence of any endotherm corresponding to the melting temperature of the aryloxysilane polymer from bisphenol-A suggests that this polymer is amorphous.

The technique described in 5.2.3. was adopted again to detect the evolution of volatile materials. The response of the Pirani gauge which monitors the presence of volatile

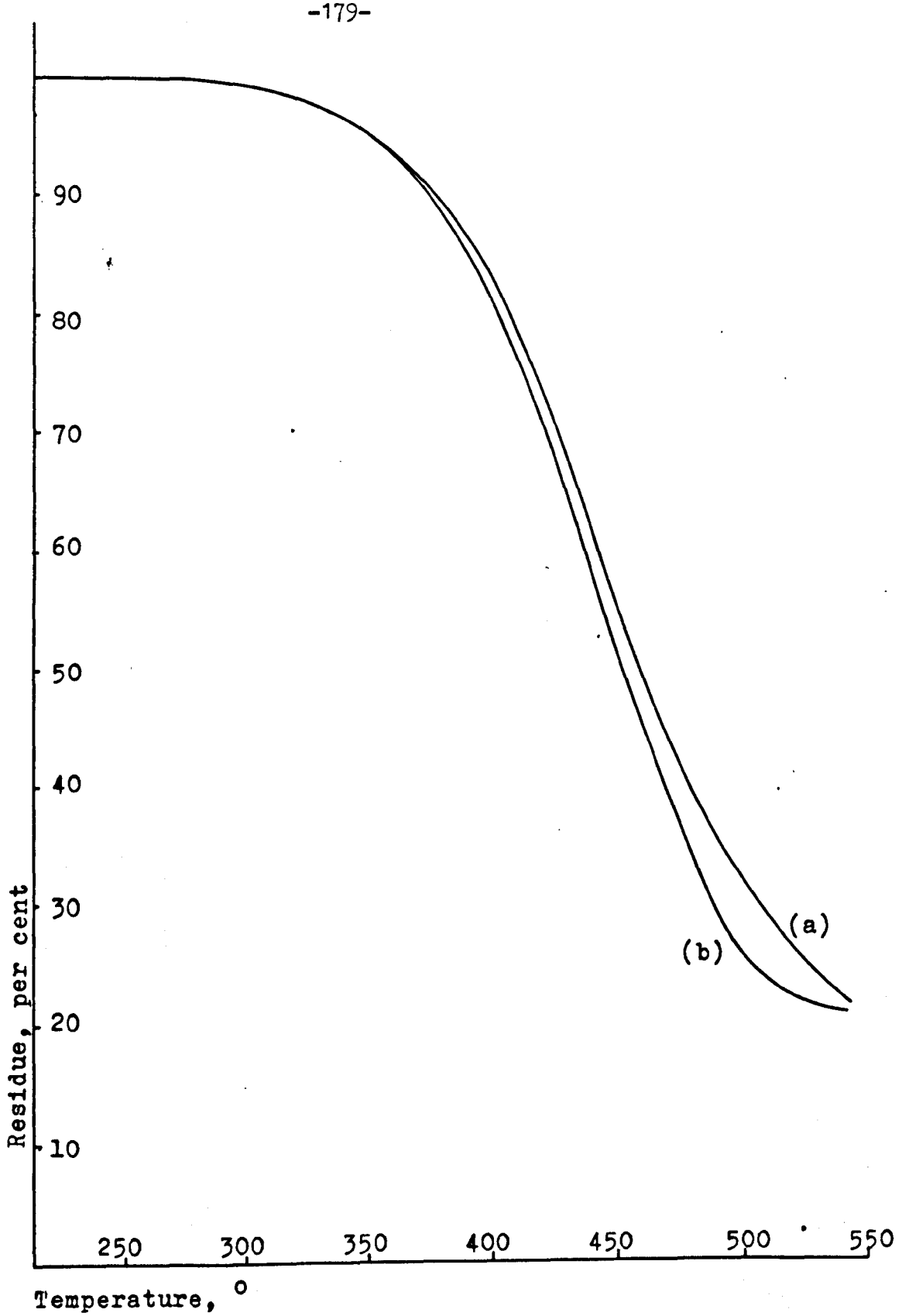


Fig. 7.3 TG traces for aryloxysilane polymers from: a) bisphenol A; b) hydroquinone.

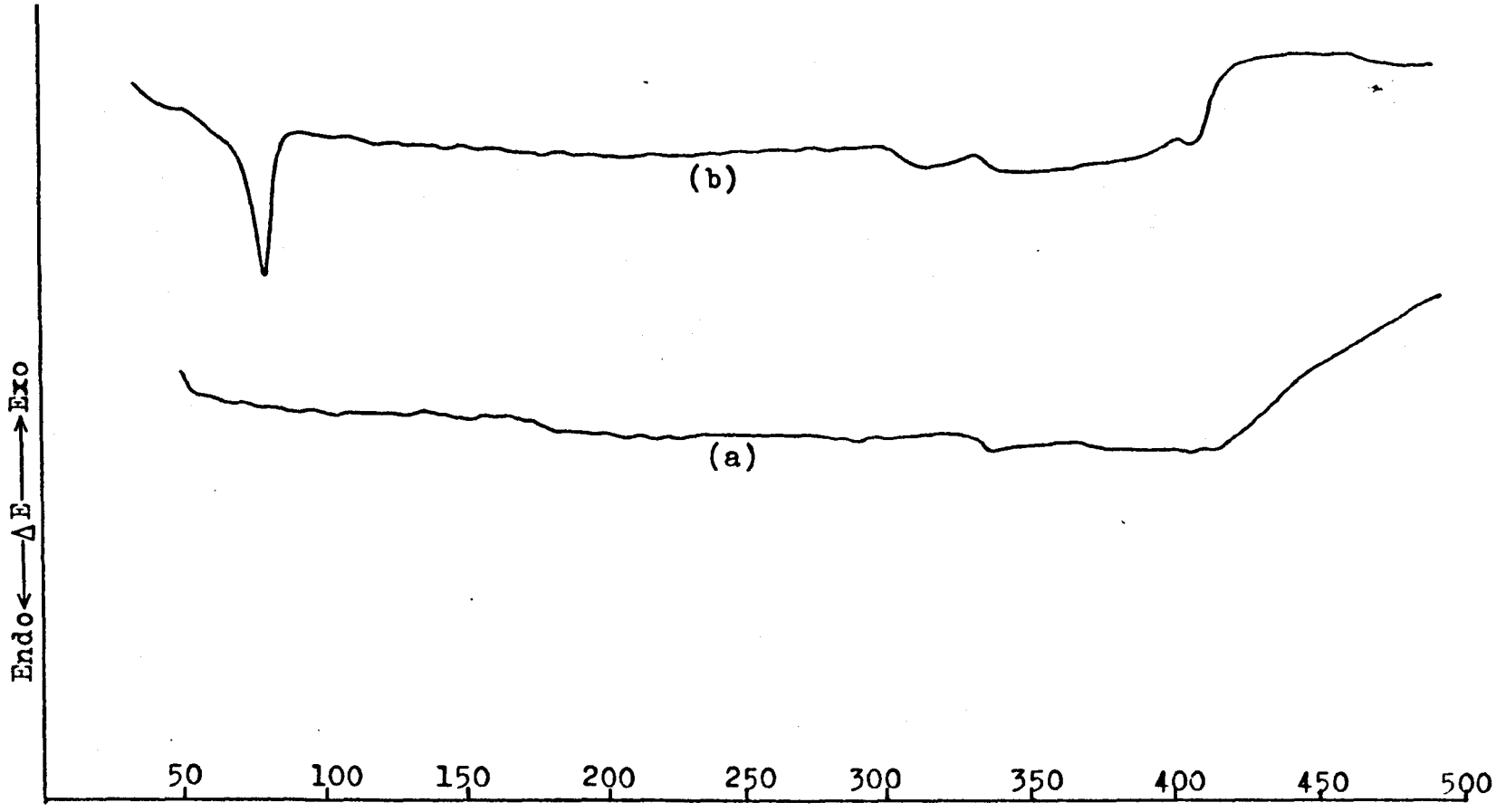


Fig. 7.4 DSC traces for aryloxysilane polymers from: a) bisphenol A; b) hydroquinone.

materials as they are formed is illustrated in Figure 7.5 for both polymers. The formation of gaseous material commences at 275° when the polymer from hydroquinone is degraded. However the corresponding polymer prepared from bisphenol-A gave no sign of volatile formation until 410°. No non-condensable products were detected. In both cases hexamethylcyclotrisiloxane was identified from the infrared analysis (Fig. 7.6) as the sole gaseous product.

Prolonged heating at 500° results in 100% weight loss which apart from the hexamethylcyclotrisiloxane formation, may be accounted for by the "cold ring" fraction. No visible differences were detected in the infrared spectra from "cold ring" fractions collected after degrading at 400°, 450° or 500° (Fig. 7.7 and 7.8). When compared with the spectra of the original polymers, it was noted that no new bands appear or existing bands disappear upon degrading to form "cold ring" fraction. However in the polymer from bisphenol-A the relative intensities of the Si-O absorption bands at 1240-1210 cm^{-1} and between 1100 and 1000 cm^{-1} decrease slightly.

7.5 Discussion

Comparison of data from TG, TVA and isothermal degradations suggest that the aryloxysilane polymers are thermally less stable than the silphenylene-siloxane polymers. However TG demonstrates that the weight loss behaviour is very similar to that of a hydroxyl terminated DMS with a number average molecular weight of 94500 (Ref 3).

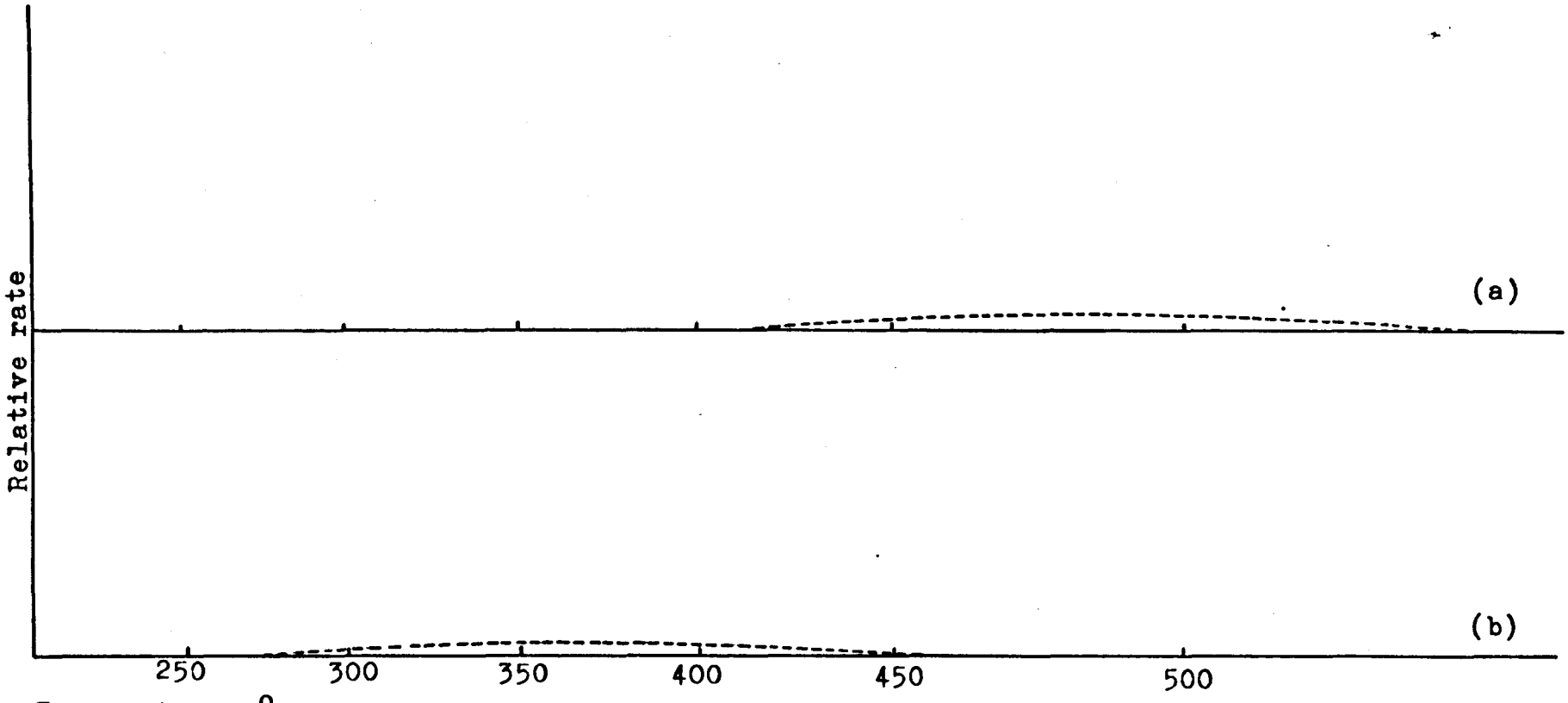


Fig. 7.5 TVA traces for aryloxysilane polymers from: a) bisphenol A; b) hydroquinone. Heating rate $10^{o}min^{-1}$ from ambient to 500^{o} and thereafter held at 500^{o}.

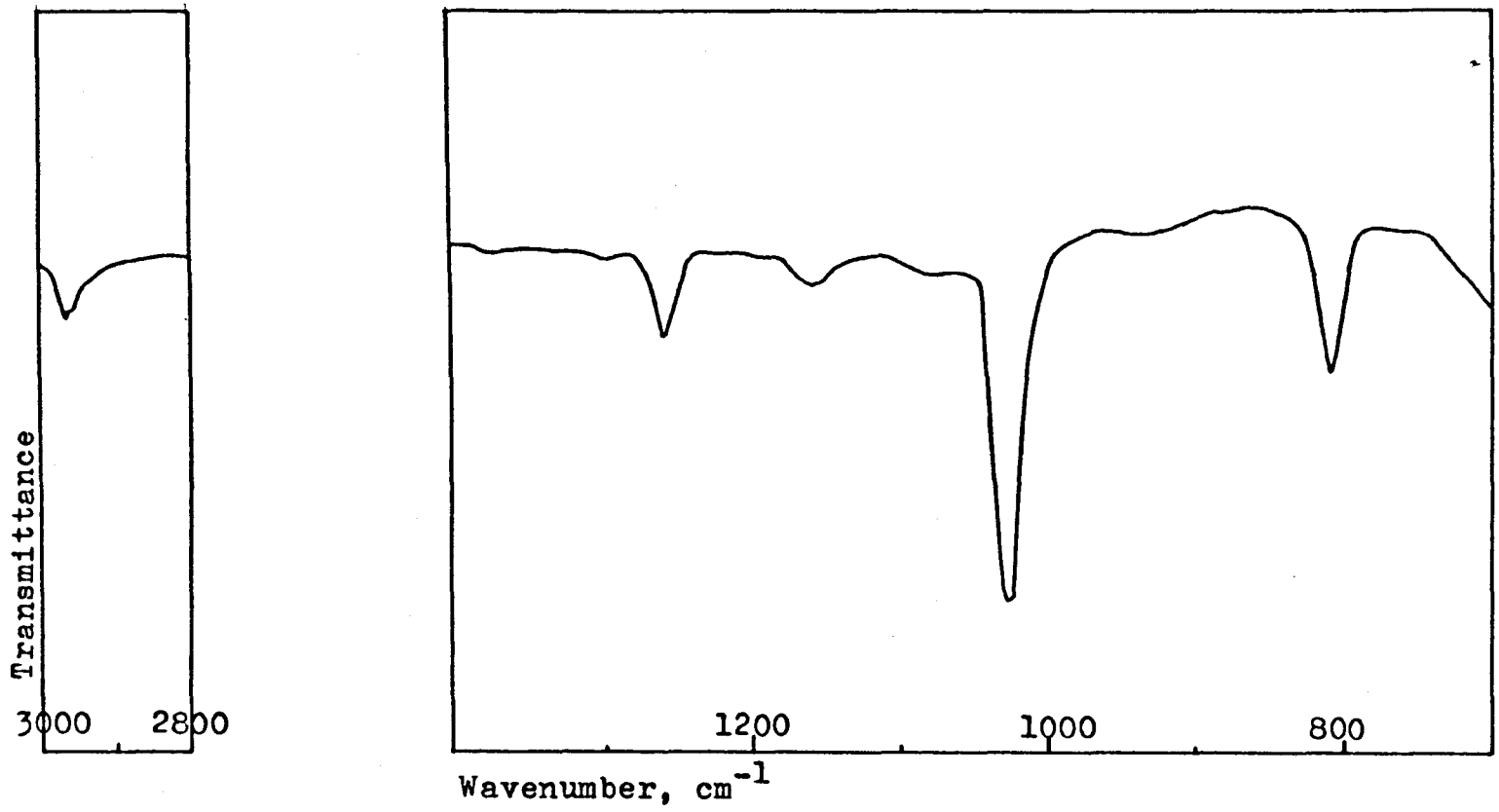


Fig. 7.6 Infrared spectrum of the gaseous products from each aryloxysilane polymer.

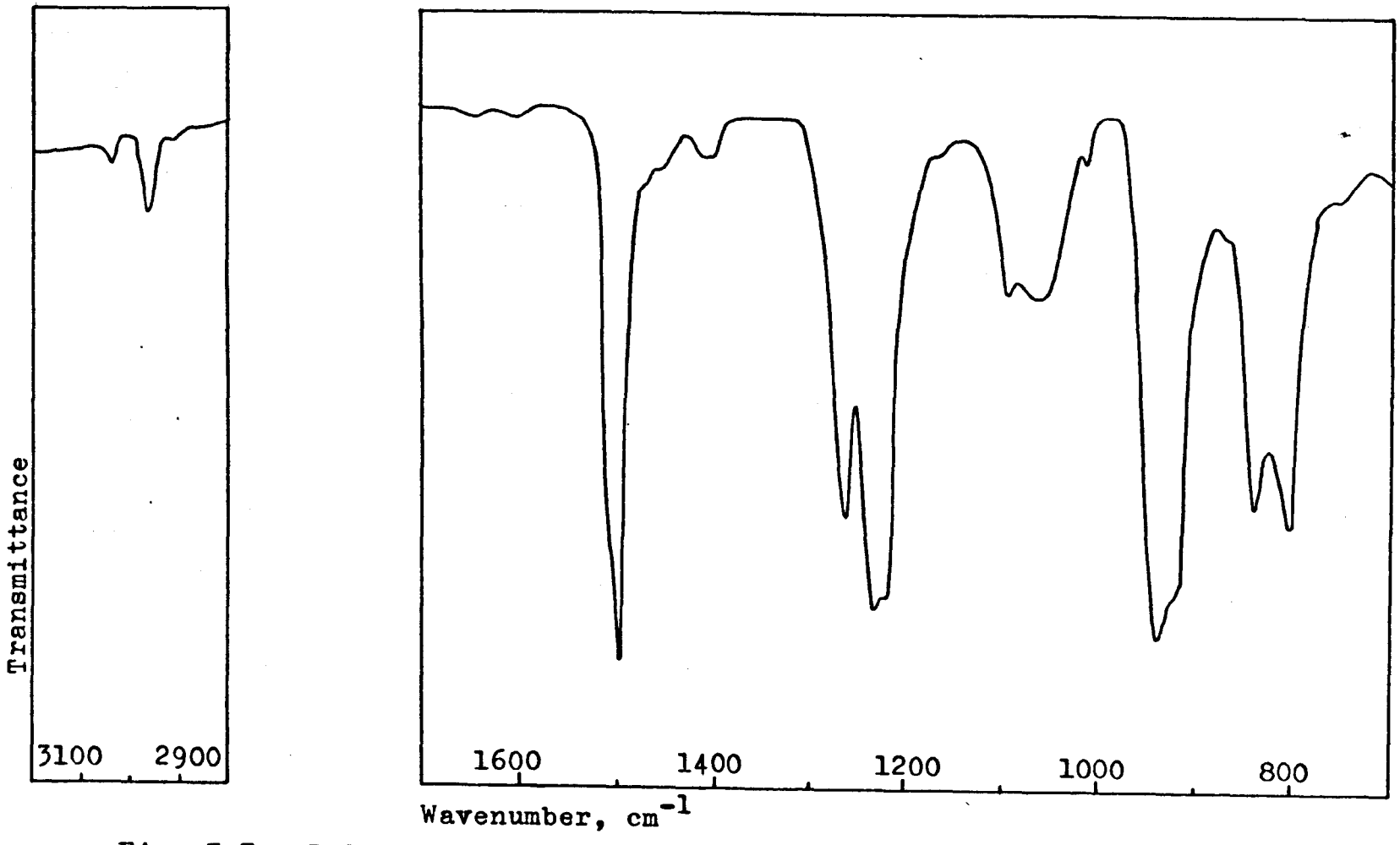


Fig. 7.7 Infrared spectrum of 'cold ring' fraction from the hydroquinone polymer.

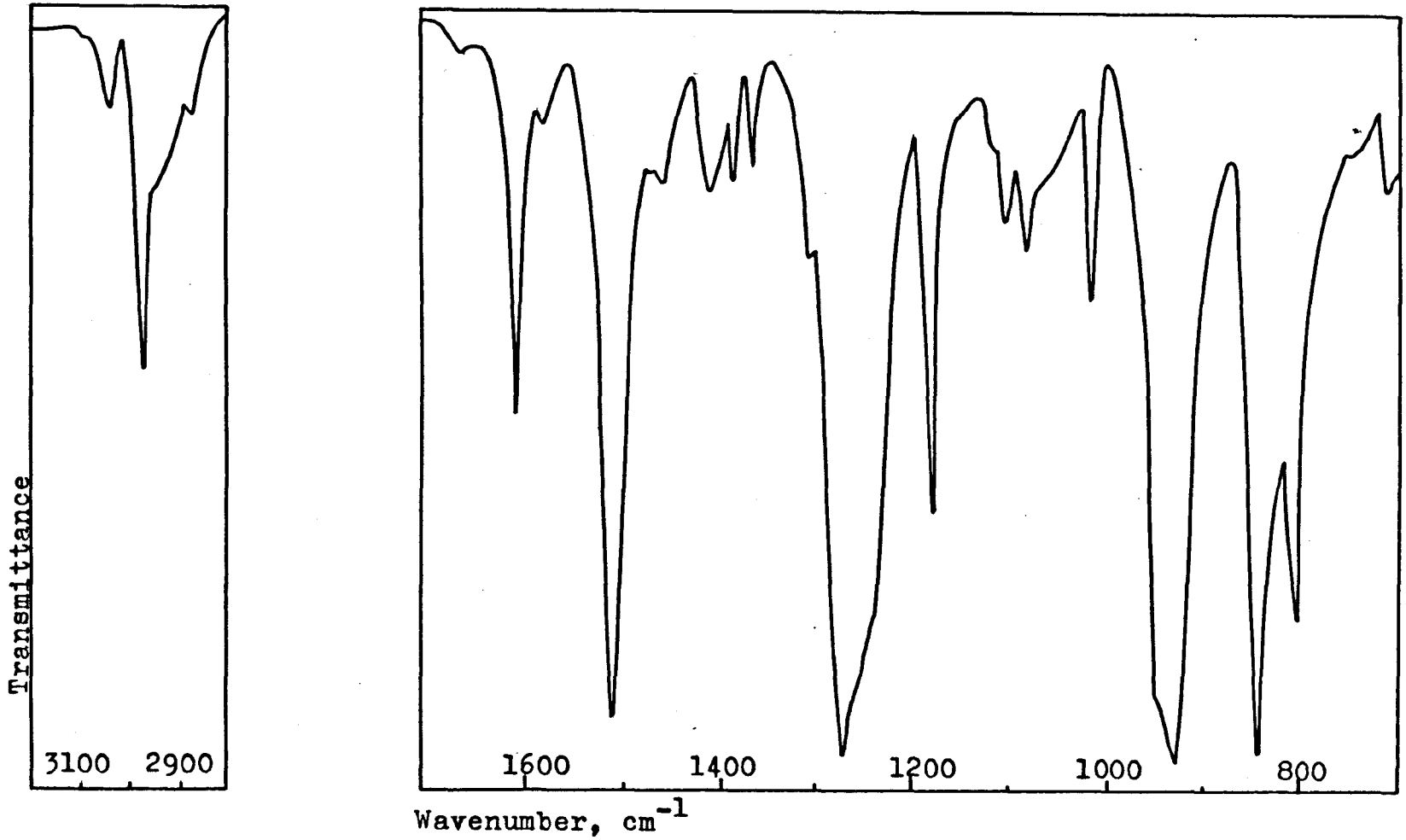
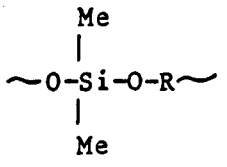


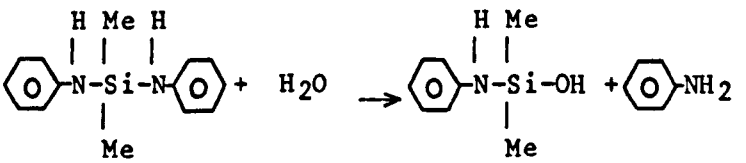
Fig. 7.8 Infrared spectrum of 'cold ring' fraction from the bisphenol A polymer.

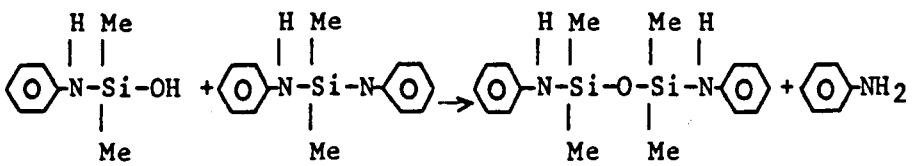
The production of hexamethylcyclotrisiloxane, common to both the degradation of DMS (Ref 3) and TMPS, was again detected here. An intermolecular mechanism was proposed to account for the formation of cyclic siloxane in the decomposition of TMPS (Ref 26) while that suggested for DMS is intramolecular (Ref 6). If the structure of the aryloxysilane polymer truly consists of oxygen atoms separated alternately by either a silicon atom or an arylene group:



R = arylene group

then the intermolecular mechanism would appear to be more reasonable. However the possibility of water present in the polymerization must be considered as this could result in hydrolysis of the dianilinosilane to the silanol which on reacting further would result in the formation of the siloxane unit:





The presence of several siloxane units together may allow the formation of the cyclic compound via the intramolecular process. Detection of the formation of Si-O-Si units is prevented by the coincidence of the Si-O-Si absorption with

the asymetric Si-O-C stretch absorption at 1000-1100 cm^{-1}.

The similarity of the spectra of the "cold ring" fraction to that of the original polymer suggests that low molecular weight oligomers form the bulk of the breakdown products, their structures being similar to the structure of the starting material. This suggests that breakdown involves the main polymer chain.

Prolonged isothermal heating of the aryloxysilane polymers results in 100% weight loss which resembles more the behaviour of DMS (Ref 3) than TMPS. Results from TG, published by Curry and Byrd (Ref 55), of corresponding diphenyl substituted polymers demonstrated that the temperature at which weight loss commences is higher and an appreciable quantity of residue remained. It appears that chain branching is absent in the aryloxysilanes when the silicon atoms are dimethyl substituted but is induced when phenyl groups are present. The increased stability observed for the phenyl substituted polymers may be due to chain branching stabilising the polymer. Alternatively the decomposition may be hindered by the large size of the phenyl group.

7.6 Suggestions for Future Work

Modification of the aryloxysilane structure may be achieved in several different ways. The effect of the nature of organic group attached to silicon or altering the diol used in the polymerisation would be interesting. Also a more thorough investigation into the mechanism of degradation would be advantageous to the understanding of the effect of these and other alterations.

The low thermal stability of the aryloxysilane polymers relative to the silphenylene-siloxane polymers does not imply that their potential value will be reduced in a similar manner. Good resistance to heat is just one of many criteria which determine that a polymer has some commercial worth. A more comprehensive study of both the physical properties of the polymer and the dependence of these properties on temperature is essential. The widespread applicability of DMS, which has similar stability to heat (Ref 3), illustrates that further research into the aryloxysilane polymers may be worthwhile.

CHAPTER 8

A COMPARISON OF POLYSILOXANES WITH METHYL OR PHENYL SUBSTITUTED SILICON ATOMS AND p-SILPHENYLENE UNITS IN THE MAIN SILOXANE CHAIN.

8.1. Introduction

The products from the thermal degradation of DMS and poly(methylphenylsiloxane) have been identified and their formation discussed from a mechanistic point of view (Ref 3, 10). Similar investigations concerning silphenylene-siloxane polymers with either methyl or phenyl substituents on the silicon atoms and varying silphenylene content were described in the preceding chapters of this thesis. The nature of the products formed and the mechanisms involved in the degradation of these siloxane related polymers will be discussed in relation to the effect of the different substituents and the concentration of silphenylene units.

8.2. Discussion

Basically two mechanisms appear to be involved in the thermal degradation of the silphenylene-siloxane polymers. Below 450° the mechanism involves rearrangement of the main polymer chain. As the temperature is increased direct bond scission becomes the initial step. The aromatic content of the polymer is seen to influence which mechanism is dominant.

The thermal decomposition of DMS under vacuum yields a continuous mixture of cyclic oligomers from trimer upwards. Evolution of volatiles from this siloxane polymer, where the substituents are relatively small and the chain flexible,

begins at 350° in a structural rearrangement. Prolonged heating at this temperature will result in 100% weight loss which may all be accounted for by the cyclic oligomers.

Introducing phenyl substituents on the silicon atoms or replacing the oxygen atoms in part by p-phenylene groups restricts the formation of cyclic compounds probably by reducing the flexibility of the chain. Thus poly(methylphenylsiloxane) and the silphenylene-siloxane polymers show higher threshold temperatures to weight loss via the formation of cyclic oligomers. Throughout the series of silphenylene-siloxane copolymers, both the quantity and range of cyclic oligomers produced decrease with increasing p-phenylene content. The mechanism for the formation of the cyclic compounds is similar throughout and involves rearrangement of the siloxane bonds. Although this is usually thought to be an intramolecular process, an intermolecular mechanism was invoked for those silphenylene-siloxane copolymers with high silphenylene content.

Evidence of other reactions occurring when either the silphenylene-siloxane polymers or hydroxyl terminated poly(methylphenylsiloxane) are heated isothermally at the lower temperatures of degradation is seen from the development of insolubility in the residue. In poly(methylphenylsiloxane) this change is accompanied by the production of benzene. A mechanism in which the hydroxyl terminals participate in the cleavage of the Si-Ph bond, resulting in benzene production and a branched structure, was suggested (Ref 10). However in the silphenylene-siloxane polymers a similar mechanism serves

only to modify the polymer end-groups. An alternative mechanism involving rearrangement of Si-Me and Si-O bonds was proposed. This results in the formation of a branched structure without the loss of volatile material.

Values for the rate of chain branching were calculated experimentally by sol-gel analysis. These results were used in a relative comparison only, since the effect of the evolution of volatile material throughout the process was not taken into account. However from these results it appears that the rate of crosslinking is directly proportional to the silphenylene content. The largest value for the rate of crosslinking was calculated for MPPS. This is not surprising in view of the fact that this polymer contains both phenyl substituents and p-phenylene units in the main chain. Chain branching may thus result from both of the above mechanisms. No evidence for the formation of cyclic compounds was detected in the degradation of MPPS.

The mechanism involving direct bond scission occurs only at the higher temperatures of degradation and apparently involves cleavage of the Si-C_{aryl} bond. The nature of the volatile products formed at this stage in the degradation depends on whether bond scission occurs within the polymer backbone at a silphenylene unit or between a silicon atom and its phenyl substituent. In the former case a series of short chain oligomers with either Si-H or Si H end-groups are found in the volatile fraction of the products. Poly(methylphenylsiloxane) on the other hand yields benzene and two bicyclic compounds where the bridging units are

thought to be methylene groups (Ref 10). Although MPPS contains both p-phenylene units in the main chain and phenyl substituents, only linear compounds and benzene were detected in the gaseous products and the "cold ring" fraction. The absence of cyclic oligomers throughout the degradation of MPPS suggests that their formation is sterically unfavourable due to the high benzene ring content in the polymer.

Another feature common to those siloxane polymers which undergo direct bond scission is the formation of an insoluble residue. It is suggested that this is a result of the recombination of the different types of radicals formed either in the primary bond scission reaction or in rearrangement processes which follow the initial bond cleavage.

Comparative studies of the thermal stabilities of DMS (Ref 3) and poly(methylphenylsiloxane) (Ref 10) reveal that the replacement of dimethyl by methylphenyl substituted silicon atoms leads to an enhancement of the thermal stability. Similar behaviour was witnessed in the silphenylene-siloxane polymers when MPPS is compared to TMPS. However further replacement of methyl groups by phenyl groups to give poly(diphenylsiloxane) (Ref 17) or TPPS does not result in additional thermal stability. The difficulties encountered in their preparation resulted in the formation of low molecular weight polymers only. A brief investigation of the behaviour of these low molecular weight polymers when subjected to heat demonstrated that they are thermally less stable than DMS.

8.3. Suggestions for Future Work

If good thermal stability was the sole criterion for a useful, synthetic polymer then, on the basis of their greater resistance to heat, the silphenylene-siloxane polymers would be expected to have more widespread application than the linear polysiloxanes. Unfortunately the assessment of the potential value of a new polymer is not thus straightforward owing to the existance of other agencies which may act upon the polymer at different stages in its life. It is important, therefore, to consider the resistance of the polymer to these other agencies which include mechanical stress, light, radiation, chemical reagents and ozone. Physical properties such as melting temperature, Tm, glass transition temperature, Tg, and crystallinity are also of prime importance. These give an indication as to whether the polymer will be glass-like, rubber-like or fibre-forming at a given temperature.

The chain flexibility is greatly reduced when the p-phenylene group is incorporated in the chain (Ref 2). This effect is demonstated for TMPS which has Tg = 20° and Tm = 155° (Ref 24) compared with DMS for which Tg = -123° and Tm = -55° (Ref 24). By varying the p-phenylene content, the degree of chain stiffness may be controlled. Evidence for this is given by the increase in the values of Tm with increasing silphenylene content observed in the DSC traces of the silphenylene-siloxane copolymers (Fig 4.2). It would appear that the insertion of silphenylene groups into the siloxane polymer not only increases the thermal stability

to weight loss but also provides a potential way of controlling the chain stiffness. Thus the silphenylene content in a silphenylene-siloxane polymer will be determined by the prospective application.

The stability and thermal degradation properties of the silphenylene-siloxane polymers suggest that they have considerable potential for future application. However, an investigation in greater depth of the physical properties and the stability to other degradative agencies is essential for a complete commercial assessment.

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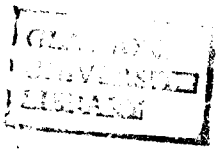

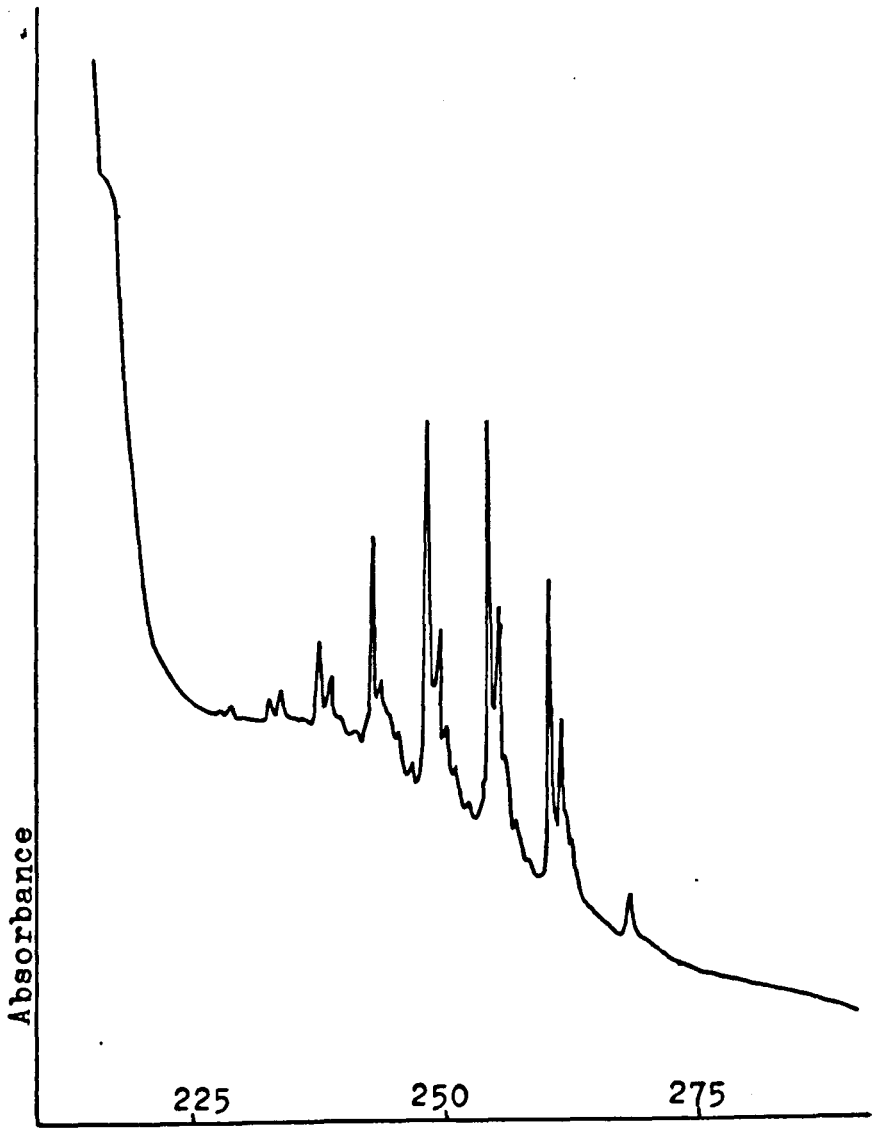

Fig. 5.6 Ultraviolet spectrum of the gaseous products from MPPS heated to 500°.